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## Preface

Welcome to *Chemistry: Atoms First 2e*, an OpenStax resource. This textbook was written to increase student access to high-quality learning materials, maintaining the highest standards of academic rigor at little or no cost.

## About OpenStax

OpenStax is a nonprofit based at Rice University, and it's our mission to improve student access to education. Our first openly licensed college textbook was published in 2012, and our library has since scaled to over 30 books for college and AP<sup>®</sup> courses used by hundreds of thousands of students. OpenStax Tutor, our low-cost personalized learning tool, is being used in college courses throughout the country. Through our partnerships with philanthropic foundations and our alliance with other educational resource organizations, OpenStax is breaking down the most common barriers to learning and empowering students and instructors to succeed.

## About OpenStax resources

### Customization

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Because our books are openly licensed, you are free to use the entire book or pick and choose the sections that are most relevant to the needs of your course. Feel free to remix the content by assigning your students certain chapters and sections in your syllabus, in the order that you prefer. You can even provide a direct link in your syllabus to the sections in the web view of your book.

Instructors also have the option of creating a customized version of their OpenStax book. The custom version can be made available to students in low-cost print or digital form through their campus bookstore. Visit the Instructor Resources section of your book page on [openstax.org](https://openstax.org) for more information.

## Errata

All OpenStax textbooks undergo a rigorous review process. However, like any professional-grade textbook, errors sometimes occur. Since our books are web based, we can make updates periodically when deemed pedagogically necessary. If you have a correction to suggest, submit it through the link on your book page on [openstax.org](https://openstax.org). Subject matter experts review all errata suggestions. OpenStax is committed to remaining transparent about all updates, so you will also find a list of past errata changes on your book page on [openstax.org](https://openstax.org).

## Format

You can access this textbook for free in web view or PDF through [openstax.org](https://openstax.org), and for a low cost in print.

## About *Chemistry: Atoms First 2e*

This text is an atoms-first adaptation of OpenStax *Chemistry 2e*. The intention of “atoms-first” involves a few basic principles: first, it introduces atomic and molecular structure much earlier than the traditional approach, and it threads these themes through subsequent chapters. This approach may be chosen as a way to delay the introduction of material such as stoichiometry that students traditionally find abstract and difficult, thereby allowing students time to acclimate their study skills to chemistry. Additionally, it gives students a basis for understanding the application of quantitative principles to the chemistry that underlies the entire course. It also aims to center the study of chemistry on the atomic foundation that

many will expand upon in a later course covering organic chemistry, easing that transition when the time arrives.

The second edition has been revised to incorporate clearer, more current, and more dynamic explanations, while maintaining the same organization as the first edition. Substantial improvements have been made in the figures, illustrations, and example exercises that support the text narrative.

## Coverage and scope

In *Chemistry: Atoms First 2e*, we strive to make chemistry, as a discipline, interesting and accessible to students. With this objective in mind, the content of this textbook has been developed and arranged to provide a logical progression from fundamental to more advanced concepts of chemical science. All of the material included in a traditional general chemistry course is here. It has been reorganized in an atoms-first approach and, where necessary, new material has been added to allow for continuity and to improve the flow of topics. The text can be used for a traditional two-semester introduction to chemistry or for a three-semester introduction, an approach becoming more common at many institutions. The goal is to provide a progressive, graduated introduction to chemistry that focuses on the fundamentally atom-focused nature of the subject. Topics are introduced within the context of familiar experiences whenever possible, treated with an appropriate rigor to satisfy the intellect of the learner, and reinforced in subsequent discussions of related content. The organization and pedagogical features were developed and vetted with feedback from chemistry educators dedicated to the project.

## Changes to the second edition

OpenStax only undertakes second editions when significant modifications to the text are necessary. In the case of *Chemistry: Atoms First 2e*, user feedback indicated that we needed to focus on a few key areas, which we have done in the following ways:

**Content revisions for clarity and accuracy.** The revision plan varied by chapter based on need. About five chapters were extensively rewritten and another twelve chapters were substantially revised to improve the readability and clarity of the narrative.

**Example and end-of-chapter exercises.** The example and end-of-chapter exercises in several chapters were subjected to a rigorous accuracy check and revised to correct any errors, and additional exercises were added to several chapters to more fully support chapter content.

**Art and illustrations.** Under the guidance of the authors and expert scientific illustrators, especially those well-versed in creating accessible art, the OpenStax team made changes to much of the art in the first edition of *Chemistry: Atoms First*. The revisions included correcting errors, redesigning illustrations to improve understanding, and recoloring for overall consistency.

**Accessibility improvements.** As with all OpenStax books, the first edition of *Chemistry: Atoms First* was created with a focus on accessibility. We have emphasized and improved that approach in the second edition. To accommodate users of specific assistive technologies, all alternative text was reviewed and revised for comprehensiveness and clarity. Many illustrations were revised to improve the color contrast, which is important for some visually impaired students. Overall, the OpenStax platform has been continually upgraded to improve accessibility.

## **Partnership with University of Connecticut and UConn Undergraduate Student Government**

*Chemistry: Atoms First 2e* is a peer-reviewed, openly licensed introductory textbook produced through a collaborative publishing partnership between OpenStax and the University of Connecticut and UConn Undergraduate Student Government Association.

## **Pedagogical foundation**

Throughout *Chemistry: Atoms First 2e*, you will find features that draw the students into scientific inquiry by taking selected topics a step further. Students and educators alike will appreciate discussions in these feature boxes.

**Chemistry in Everyday Life** ties chemistry concepts to everyday issues and real-world applications of science that students encounter in their lives. Topics include cell phones, solar thermal energy power plants, plastics recycling, and measuring blood pressure.

**How Sciences Interconnect** feature boxes discuss chemistry in context of its interconnectedness with other scientific disciplines. Topics include neurotransmitters, greenhouse gases and climate change, and proteins and enzymes.

**Portrait of a Chemist** features present a short bio and an introduction to the work of prominent figures from history and present day so that students can see the “faces” of contributors in this field as well as science in action.

## Comprehensive art program

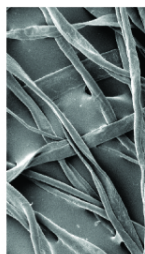
Our art program is designed to enhance students’ understanding of concepts through clear, effective illustrations, diagrams, and photographs.



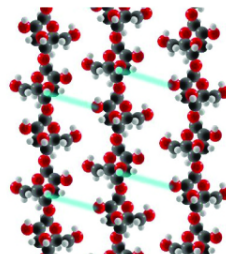
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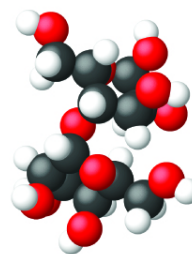
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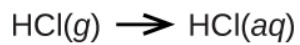
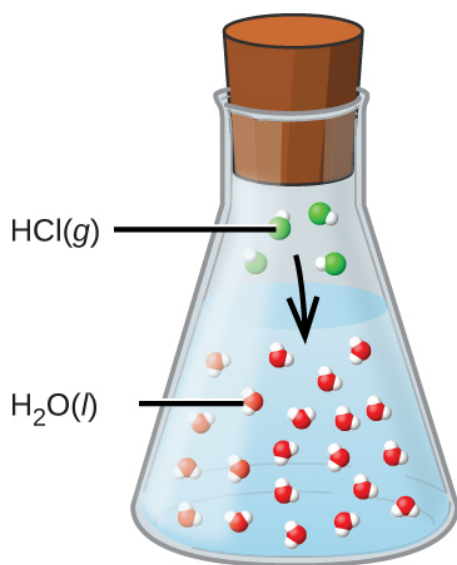
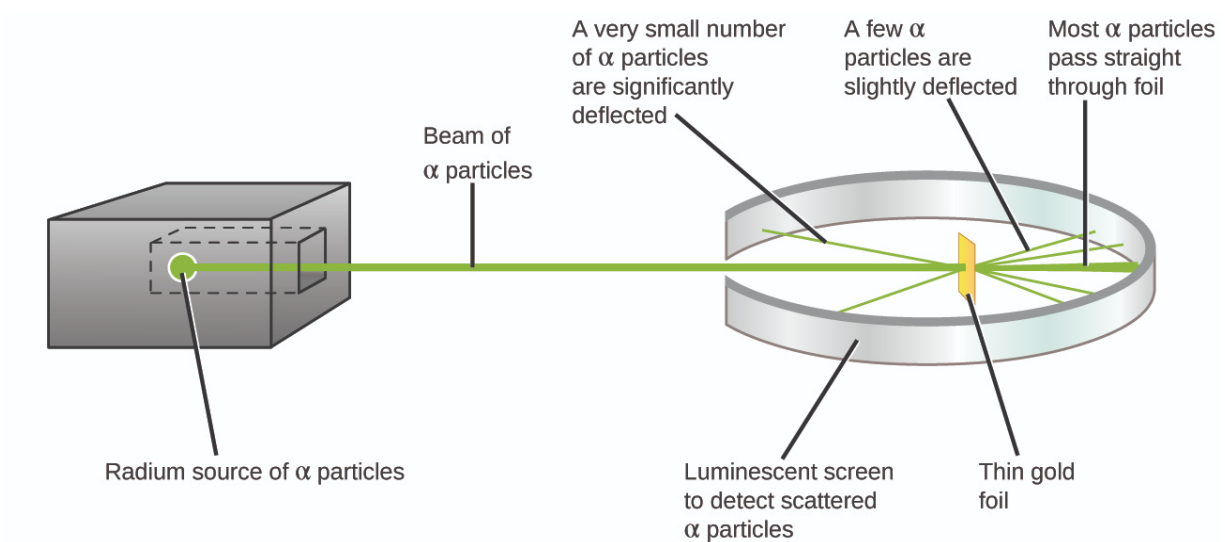
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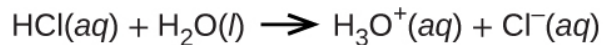
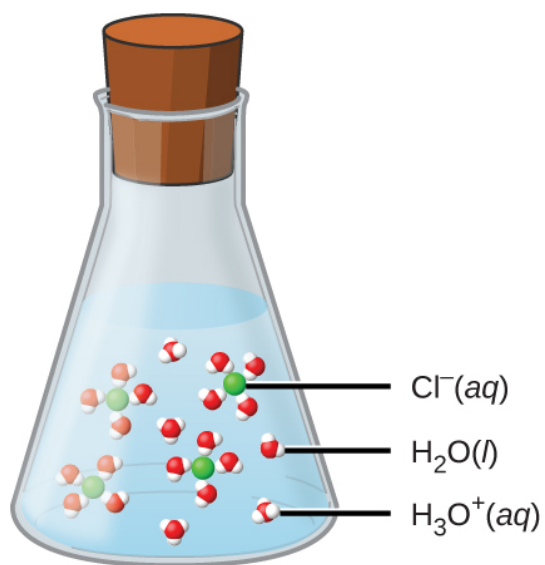
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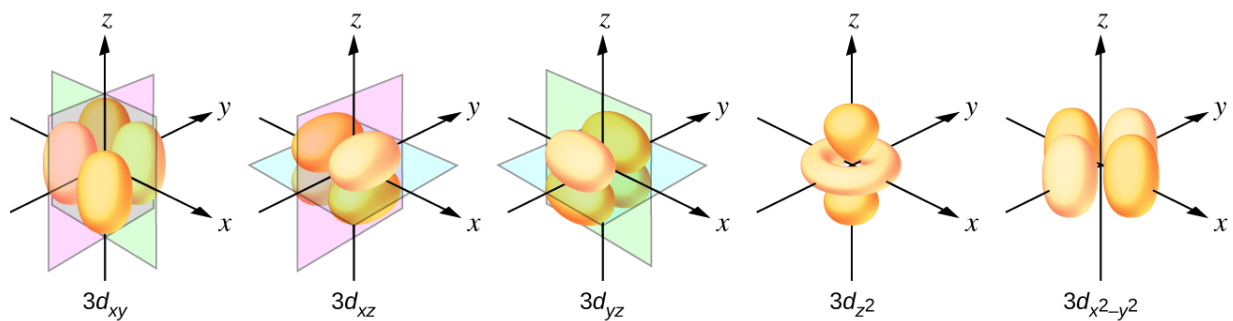
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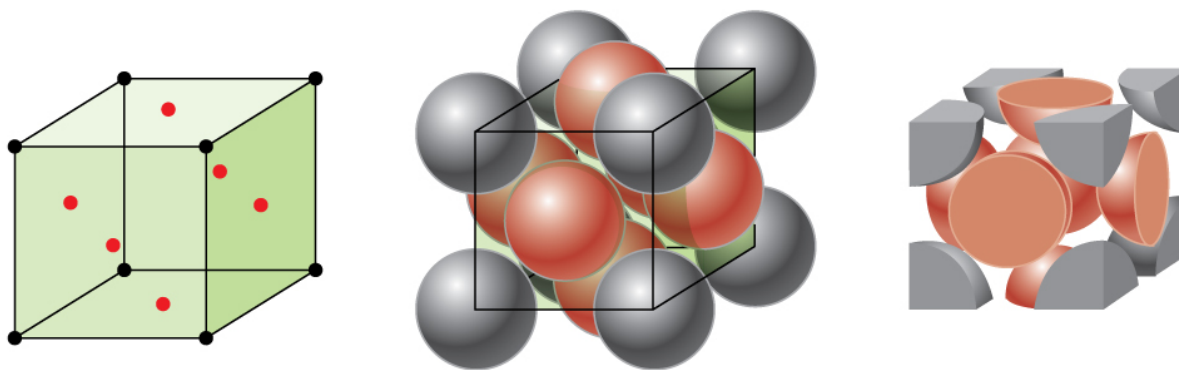
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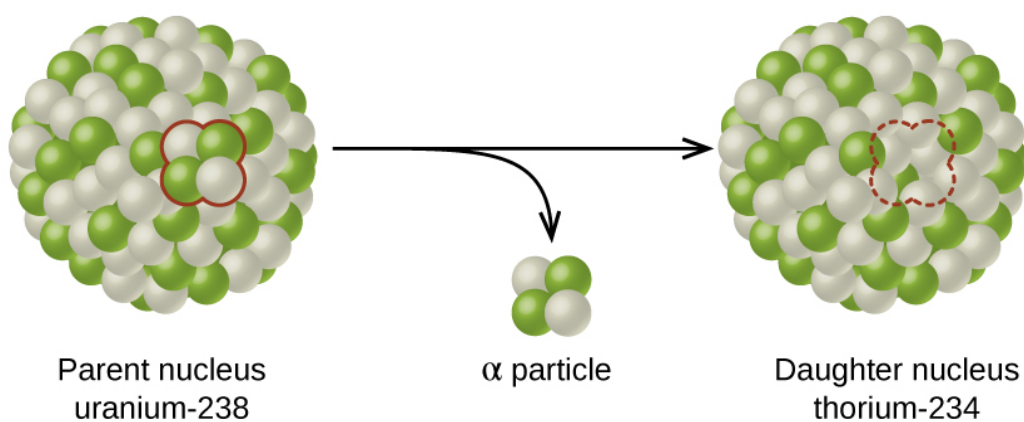
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## Interactives that engage

*Chemistry: Atoms First 2e* incorporates links to relevant interactive exercises and animations that help bring topics to life through our **Link to Learning** feature. Examples include:

PhET simulations  
IUPAC data and interactives  
TED talks

## Assessments that reinforce key concepts



In-chapter **Examples** walk students through problems by posing a question, stepping out a solution, and then asking students to practice the skill with a “Check Your Learning” component. The book also includes assessments at the end of each chapter so students can apply what they’ve learned through practice problems.

## **Additional resources**

### **Student and instructor resources**

We’ve compiled additional resources for both students and instructors, including Getting Started Guides, PowerPoint slides, and an instructor answer guide. Instructor resources require a verified instructor account, which you can apply for when you log in or create your account on [openstax.org](https://openstax.org). Take advantage of these resources to supplement your OpenStax book.

### **Community Hubs**

OpenStax partners with the Institute for the Study of Knowledge Management in Education (ISKME) to offer Community Hubs on OER Commons—a platform for instructors to share community-created resources that support OpenStax books, free of charge. Through our Community Hubs, instructors can upload their own materials or download resources to use in their own courses, including additional ancillaries, teaching material, multimedia, and relevant course content. We encourage instructors to join the hubs for the subjects most relevant to your teaching and research as an opportunity both to enrich your courses and to engage with other faculty.

To reach the Community Hubs, visit [www.oercommons.org/hubs/OpenStax](https://www.oercommons.org/hubs/OpenStax).

### **Technology partners**

As allies in making high-quality learning materials accessible, our technology partners offer optional low-cost tools that are integrated with OpenStax books. To access the technology options for your text, visit your book page on [openstax.org](https://openstax.org).

## **About the University of Connecticut**

The University of Connecticut is one of the top public research universities in the nation, with more than 30,000 students pursuing answers to critical questions in labs, lecture halls, and the community. Knowledge exploration throughout the University's network of campuses is united by a culture of innovation. An unprecedented commitment from the state of Connecticut ensures UConn attracts internationally renowned faculty and the world's brightest students. A tradition of coaching winning athletes makes UConn a standout in Division I sports and fuels our academic spirit. As a vibrant, progressive leader, UConn fosters a diverse and dynamic culture that meets the challenges of a changing global society.

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## Introduction

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- Chemistry in Context
- Phases and Classification of Matter
- Physical and Chemical Properties
- Measurements
- Measurement Uncertainty, Accuracy, and Precision
- Mathematical Treatment of Measurement Results
- Module for Testing Functions of Various Items to See How They Generate in the PDF

Chemical  
substances and  
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fabricating  
electronic devices,  
enabling  
transportation, and  
much more.

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Your alarm goes off and, after hitting “snooze” once or twice, you pry yourself out of bed. You make a cup of coffee to help you get going, and then you shower, get dressed, eat breakfast, and check your phone for messages. On your way to school, you stop to fill your car’s gas tank, almost making you late for the first day of chemistry class. As you find a seat in the classroom, you read the question projected on the screen: “Welcome to class! Why should we study chemistry?”

Do you have an answer? You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you

will learn many of the essential principles underlying the chemistry of modern-day life.



## Chemistry in Context

By the end of this module, you will be able to:

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys—for example, copper and tin were mixed together to make bronze—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations was spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform “base metals”

such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life ([link](#)).



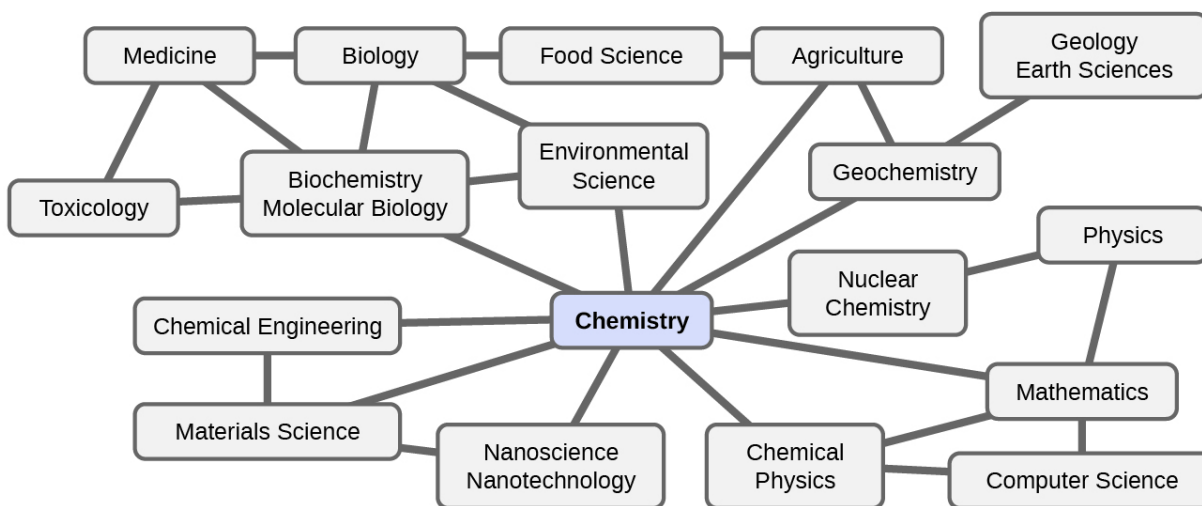
This portrayal shows an alchemist's workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation)

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter.

## **Chemistry: The Central Science**

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many

other fields ([link](#)). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world's population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.



Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

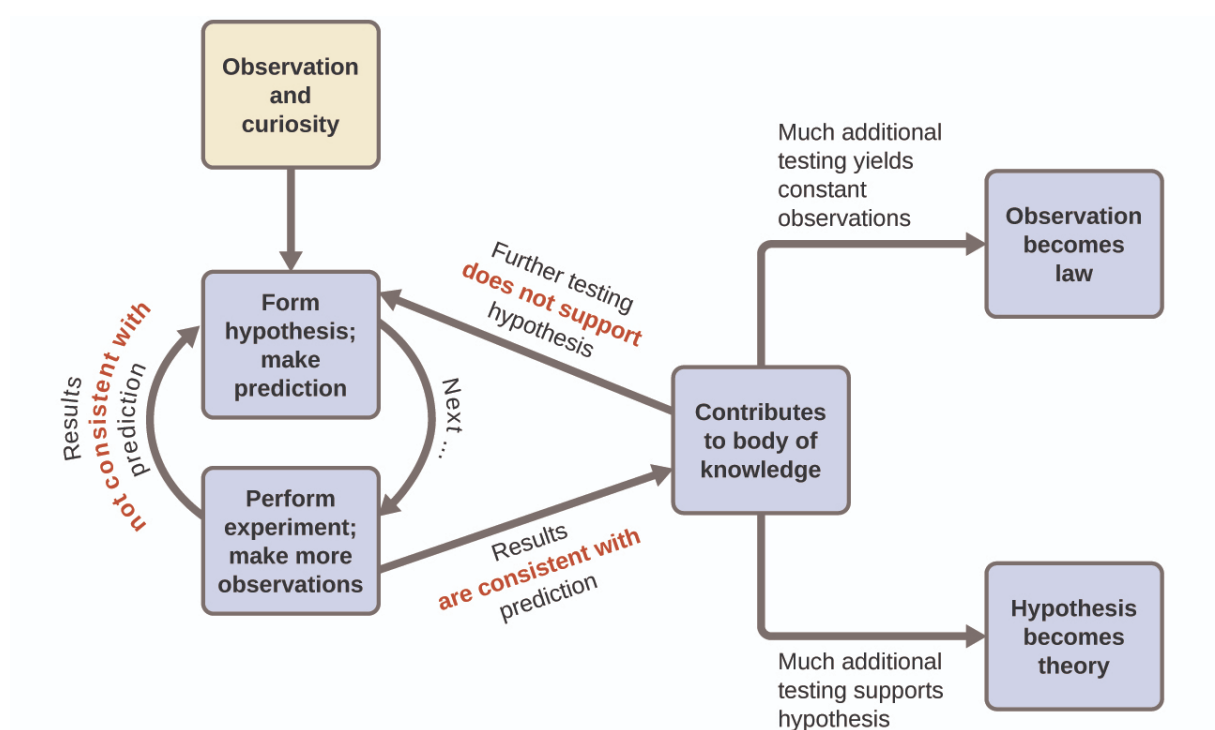
What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes and how they occurred, their causes, the changes in energy that accompany them, and the principles and laws involved. As you learn about these things, you will be learning **chemistry**, the study of the composition, properties, and interactions of matter. The practice of chemistry is not limited to chemistry books or laboratories: It happens whenever someone is involved in changes in matter or in conditions that may lead to such changes.

## The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve a **hypothesis**, a tentative explanation of observations that acts as a guide for gathering and checking information. A hypothesis is tested by experimentation, calculation, and/or comparison with the experiments of others and then refined as needed.

Some hypotheses are attempts to explain the behavior that is summarized in laws. The **laws** of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific **theories** are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available. The

path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the **scientific method** ([link](#)).



The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

## The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behavior.

*Macro* is a Greek word that means “large.” The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes everyday and laboratory chemistry, where we observe and measure physical and chemical properties such as density, solubility, and flammability.

*Micro* comes from Greek and means “small.” The **microscopic domain** of chemistry is often visited in the imagination. Some aspects of the microscopic domain are visible through standard optical microscopes, for example, many biological cells. More sophisticated instruments are capable of imaging even smaller entities such as molecules and atoms (see [\[link\]](#) (b)).

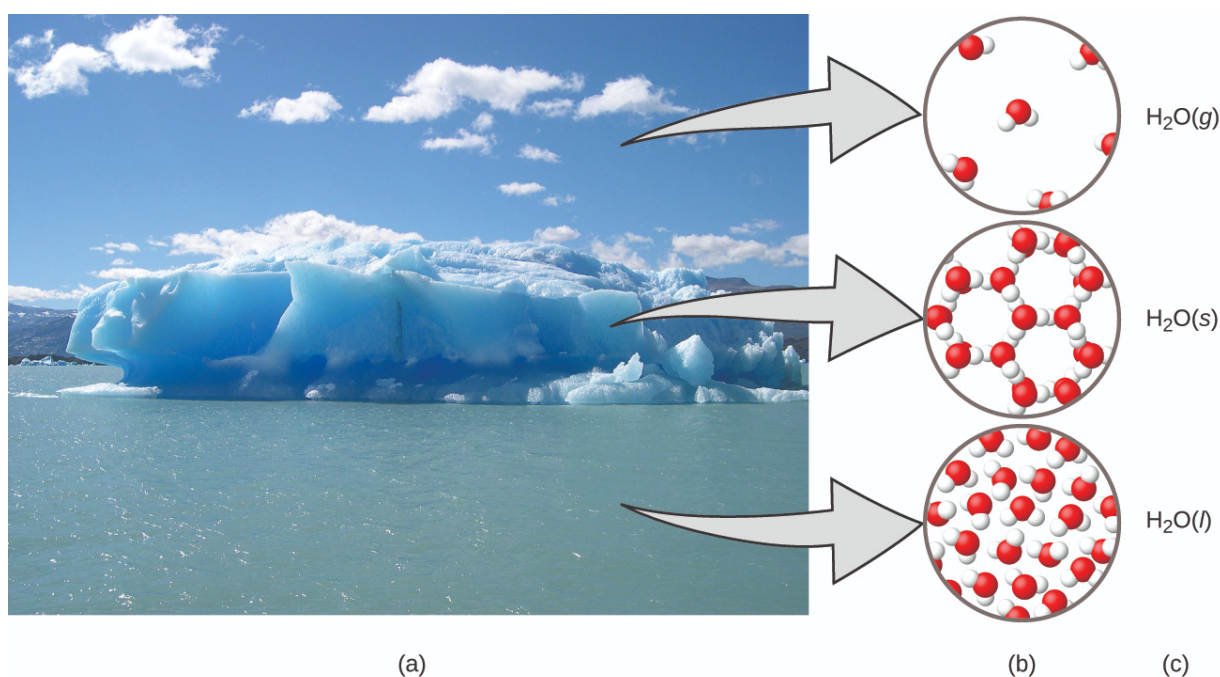
However, most of the subjects in the microscopic domain of chemistry are too small to be seen even with the most advanced microscopes and may only be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see.

The **symbolic domain** contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs, drawings, and calculations. These symbols play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures ([\[link\]](#)) are macroscopic observations.



But some properties of water fall into the microscopic domain—what cannot be observed with the naked eye. The description of water as comprising two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula  $\text{H}_2\text{O}$ , which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.



(a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula  $\text{H}_2\text{O}$  symbolizes water, and (*g*), (*s*), and (*l*) symbolize its phases. Note that clouds actually comprise either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by “Gorkaazk”/Wikimedia Commons)

## Key Concepts and Summary

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behavior of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Explain how you could experimentally determine whether the outside temperature is higher or lower than  $0^{\circ}\text{C}$  ( $32^{\circ}\text{F}$ ) without using a thermometer.

---

#### Solution:

Place a glass of water outside. It will freeze if the temperature is below  $0^{\circ}\text{C}$ .

### Exercise:

#### Problem:

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

(a) Falling barometric pressure precedes the onset of bad weather.



(b) All life on earth has evolved from a common, primitive organism through the process of natural selection.

(c) My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

**Exercise:**

**Problem:**

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

(a) The pressure of a sample of gas is directly proportional to the temperature of the gas.

(b) Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.

(c) At a higher temperature, solids (such as salt or sugar) will dissolve better in water.

---

**Solution:**

(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

**Exercise:**

**Problem:**

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

(a) The mass of a lead pipe is 14 lb.

(b) The mass of a certain chlorine atom is 35 amu.

(c) A bottle with a label that reads Al contains aluminum metal.

(d) Al is the symbol for an aluminum atom.

**Exercise:**

**Problem:**

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

(a) A certain molecule contains one H atom and one Cl atom.

(b) Copper wire has a density of about  $8 \text{ g/cm}^3$ .

(c) The bottle contains 15 grams of Ni powder.

(d) A sulfur molecule is composed of eight sulfur atoms.

---

**Solution:**

(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

**Exercise:**

**Problem:**

According to one theory, the pressure of a gas increases as its volume decreases because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behavior? Explain your answer.

**Exercise:**

**Problem:**

The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

---

**Solution:**

Macroscopic. The heat required is determined from macroscopic properties.

**Glossary**

chemistry

study of the composition, properties, and interactions of matter

hypothesis

tentative explanation of observations that acts as a guide for gathering and checking information

law

statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

macroscopic domain

realm of everyday things that are large enough to sense directly by human sight and touch

microscopic domain

realm of things that are much too small to be sensed directly

scientific method

path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

symbolic domain

specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

theory

well-substantiated, comprehensive, testable explanation of a particular aspect of nature

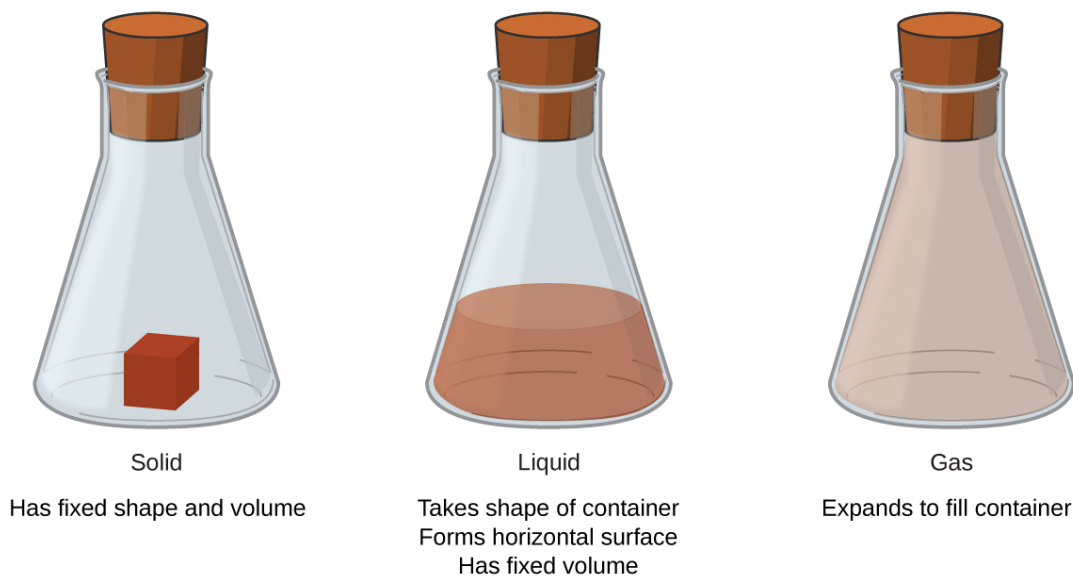
## Phases and Classification of Matter

By the end of this section, you will be able to:

- Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Distinguish between mass and weight
- Apply the law of conservation of matter
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- Define and give examples of atoms and molecules

**Matter** is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would not inflate (increase its volume) when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth ([link](#)). A **solid** is rigid and possesses a definite shape. A **liquid** flows and takes the shape of its container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A **gas** takes both the shape and volume of its container.



The three most common states or phases of matter are solid, liquid, and gas.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A **plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged

particles ([link](#)). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.



A plasma torch can be used to cut metal.  
(credit: “Hypertherm”/Wikimedia Commons)

**Note:**

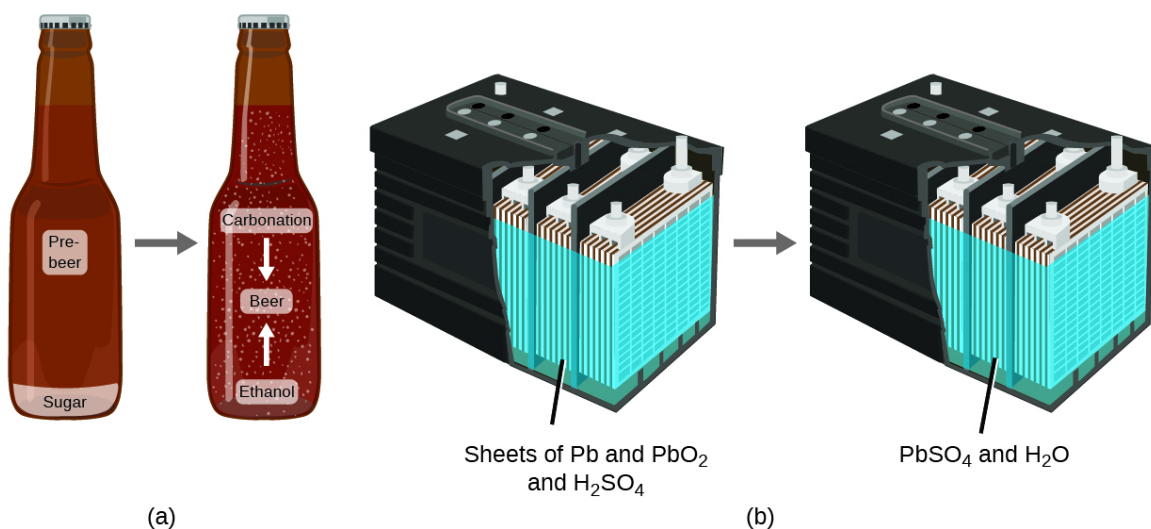
In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this [video](#) to learn more about plasma and the places you encounter it.

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter ([link](#)). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.



- (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbon dioxide. (b) The mass of the lead, lead oxide, and sulfuric acid consumed by the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

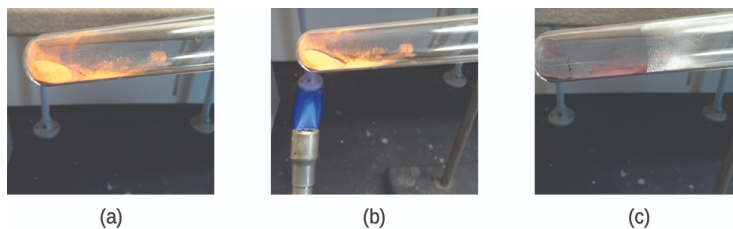
## Classifying Matter

Matter can be classified into several categories. Two broad categories are mixtures and pure substances. A **pure substance** has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

Pure substances may be divided into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called **elements**. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called **compounds**. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen ([link](#)). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).





(a) The compound mercury(II) oxide, (b) when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas.  
(credit: modification of work by Paul Flowers)

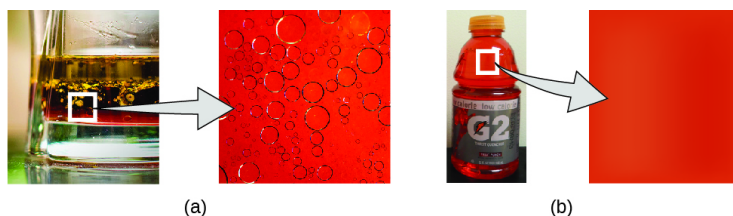
**Note:**

Many compounds break down when heated. This [site](#) shows the breakdown of mercury oxide,  $\text{HgO}$ . You can also view an example of the [photochemical decomposition of silver chloride](#) ( $\text{AgCl}$ ), the basis of early photography.

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

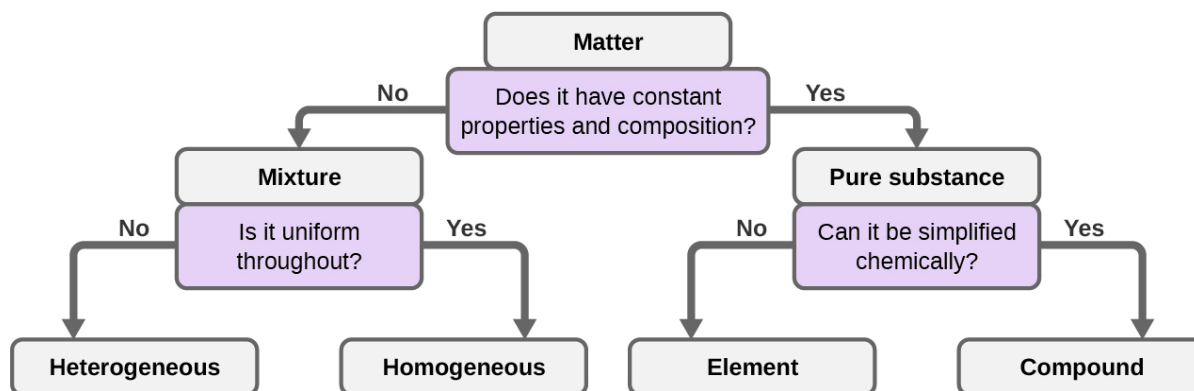
A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a **heterogeneous mixture**. Italian dressing is an example of a heterogeneous mixture ([link](#)). Its composition can vary because it may be prepared from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A **homogeneous mixture**, also called a **solution**, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly ([link](#)). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



(a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties that distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in ([link](#)).



Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

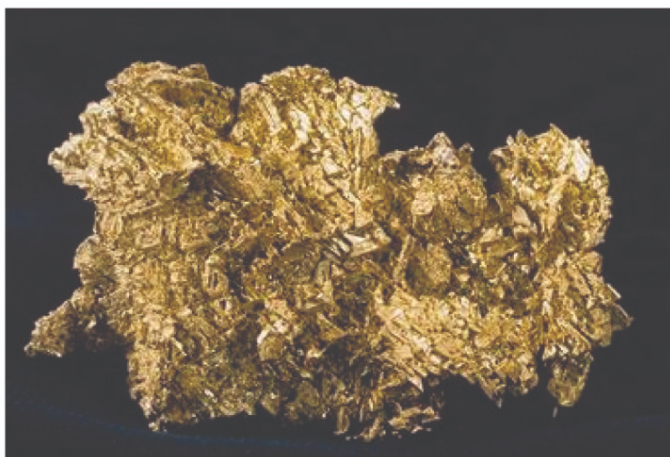
Eleven elements make up about 99% of the earth’s crust and atmosphere ([\[link\]](#)). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Elemental Composition of Earth					
Element	Symbol	Percent Mass	Element	Symbol	Percent Mass
oxygen	O	49.20	chlorine	Cl	0.19
silicon	Si	25.67	phosphorus	P	0.11
aluminum	Al	7.50	manganese	Mn	0.09
iron	Fe	4.71	carbon	C	0.08
calcium	Ca	3.39	sulfur	S	0.06
sodium	Na	2.63	barium	Ba	0.04

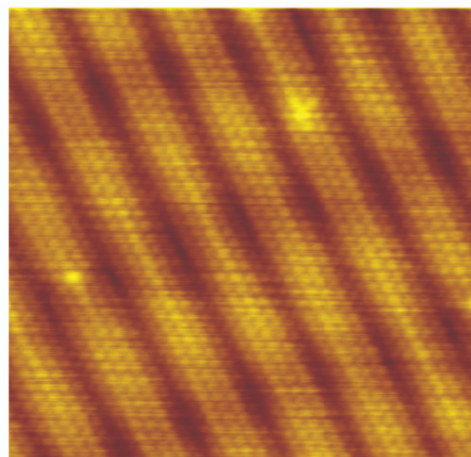
Elemental Composition of Earth					
Element	Symbol	Percent Mass	Element	Symbol	Percent Mass
potassium	K	2.40	nitrogen	N	0.03
magnesium	Mg	1.93	fluorine	F	0.03
hydrogen	H	0.87	strontium	Sr	0.02
titanium	Ti	0.58	all others	-	0.47

## Atoms and Molecules

An **atom** is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) ([link](#)). This atom would no longer be gold if it were divided any further.



(a)



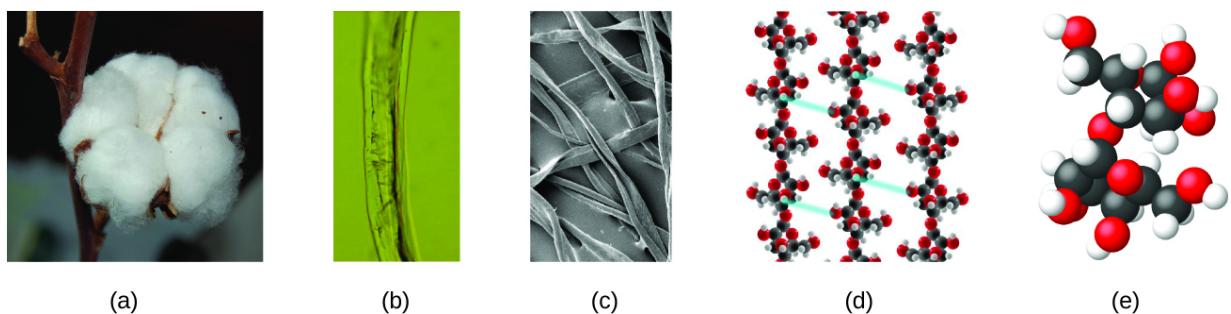
(b)

(a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by

United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry. Other aspects of Dalton’s atomic theory are still used but with minor revisions (details of Dalton’s theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom “dimes” to cover it. ([link](#)) shows increasingly close microscopic and atomic-level views of ordinary cotton.

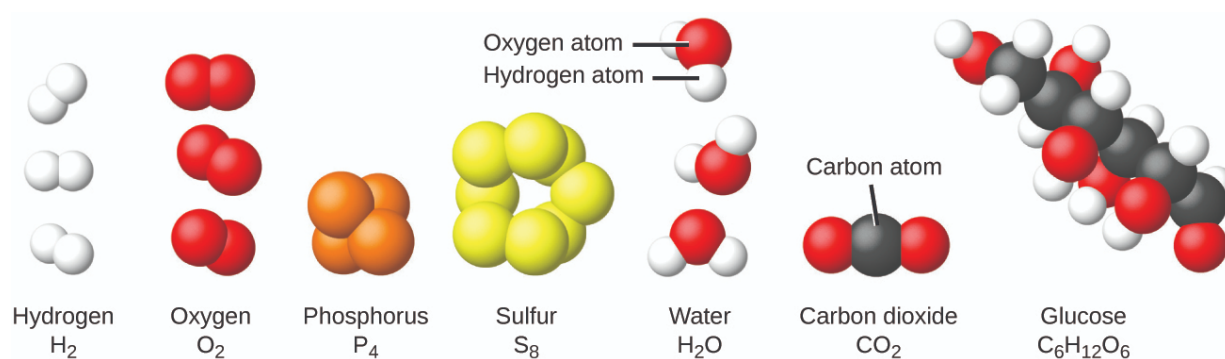


These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different

elements). (credit c: modification of work by “Featheredtar”/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about  $3 \times 10^{-13}$  grams, a mass that is far too light to be weighed on even the world’s most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or  $3 \times 10^{14}$ ) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms ([link](#)). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A **molecule** consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.



The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water,

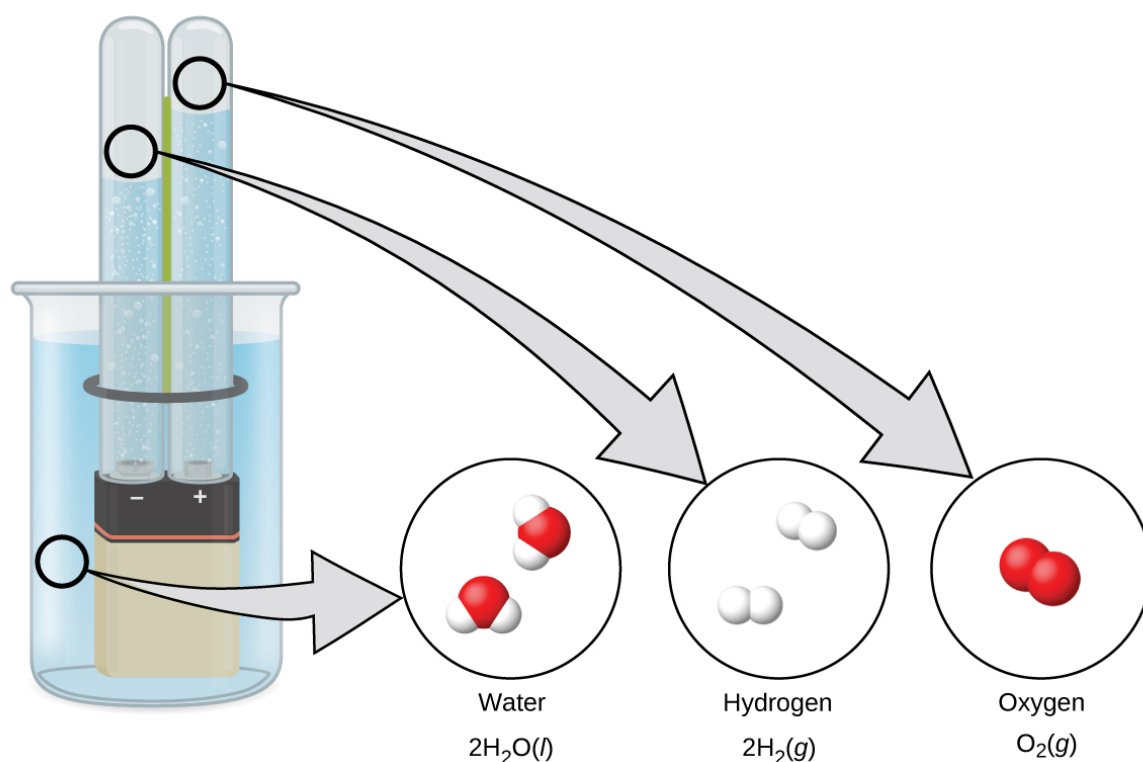


carbon dioxide, and glucose consist of combinations of atoms of different elements.

**Note:**

**Decomposition of Water / Production of Hydrogen**

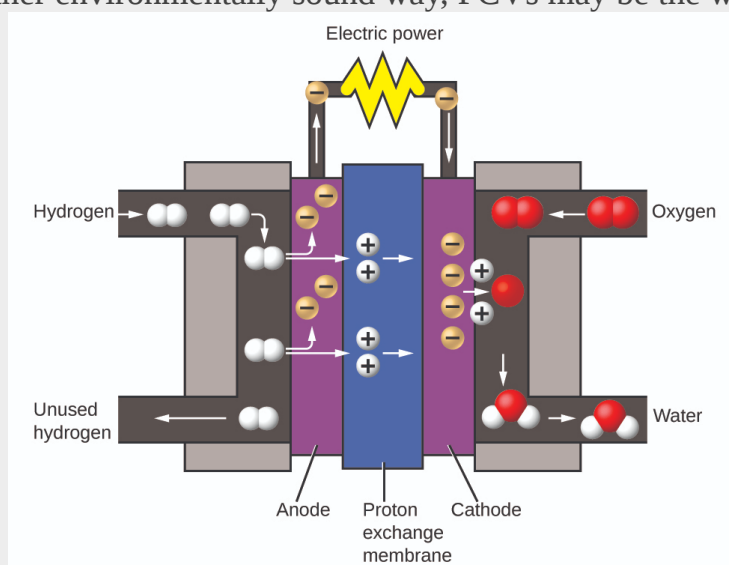
Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in ([link](#)).



The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid  $\text{H}_2\text{O}$  separates into  $\text{H}_2$  and  $\text{O}_2$  gases.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two

hydrogen molecules. The representation for what occurs,  $2\text{H}_2\text{O}(l) \longrightarrow 2\text{H}_2(g) + \text{O}_2(g)$ , will be explored in more depth in later chapters. The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline ([\[link\]](#)). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.



A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

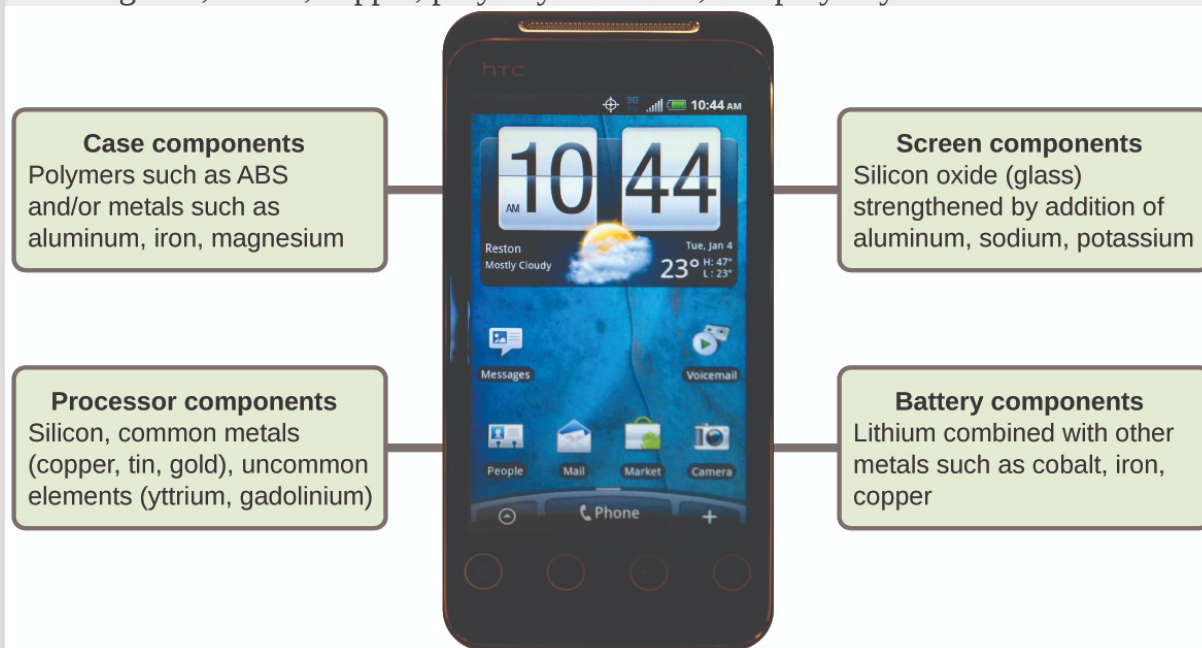
### **Note:**

#### **Chemistry of Cell Phones**

Imagine how different your life would be without cell phones ([\[link\]](#)) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in



nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers composed primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Almost one-third of naturally occurring elements are used to make a cell phone.  
(credit: modification of work by John Taylor)

## Key Concepts and Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume.

Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Why is an object's mass, rather than its weight, used to indicate the amount of matter it contains?

### Exercise:

#### Problem:

What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

---

#### Solution:

Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

### Exercise:

#### Problem:

How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

### Exercise:

#### Problem:

How does a homogeneous mixture differ from a pure substance? How are they similar?

---

#### Solution:

The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

**Exercise:**

**Problem:** How does an element differ from a compound? How are they similar?

**Exercise:**

**Problem:**

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

---

**Solution:**

Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

**Exercise:**

**Problem:**

How does an atom differ from a molecule? In what ways are they similar?

**Exercise:**

**Problem:**

Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.

---

**Solution:**

Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

**Exercise:**

**Problem:** Classify each of the following as an element, a compound, or a mixture:

(a) copper

(b) water

- (c) nitrogen
- (d) sulfur
- (e) air
- (f) sucrose
- (g) a substance composed of molecules each of which contains two iodine atoms
- (h) gasoline

**Exercise:**

**Problem:** Classify each of the following as an element, a compound, or a mixture:

- (a) iron
- (b) oxygen
- (c) mercury oxide
- (d) pancake syrup
- (e) carbon dioxide
- (f) a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom
- (g) baking soda
- (h) baking powder

---

**Solution:**

(a) element; (b) element; (c) compound; (d) mixture; (e) compound; (f) compound; (g) compound; (h) mixture

**Exercise:**

**Problem:**

A sulfur atom and a sulfur molecule are not identical. What is the difference?

**Exercise:**

**Problem:**

How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

---

**Solution:**

In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

**Exercise:****Problem:**

Why are astronauts in space said to be “weightless,” but not “massless”?

**Exercise:****Problem:**

Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

---

**Solution:**

Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

**Exercise:****Problem:**

Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.

**Exercise:**

**Problem:**

When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide called rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?

---

**Solution:**

(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

**Exercise:****Problem:**

As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:

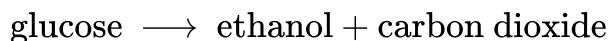
(a) Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.

(b) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.

(c) Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

**Exercise:****Problem:**

Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

**Equation:**

(a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?

(b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.

(c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

---

**Solution:**

(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

## Glossary

atom

smallest particle of an element that can enter into a chemical combination

compound

pure substance that can be decomposed into two or more elements

element

substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas

state in which matter has neither definite volume nor shape

heterogeneous mixture

combination of substances with a composition that varies from point to point

homogeneous mixture

(also, solution) combination of substances with a composition that is uniform throughout

liquid

state of matter that has a definite volume but indefinite shape

law of conservation of matter

when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass

fundamental property indicating amount of matter

matter

anything that occupies space and has mass

mixture

matter that can be separated into its components by physical means

molecule

bonded collection of two or more atoms of the same or different elements

plasma

gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance

homogeneous substance that has a constant composition

solid

state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight

force that gravity exerts on an object



## Physical and Chemical Properties

By the end of this section, you will be able to:

- Identify properties of and changes in matter as physical or chemical
- Identify properties of matter as extensive or intensive

The characteristics that distinguish one substance from another are called properties. A **physical property** is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. Some physical properties, such as density and color, may be observed without changing the physical state of the matter. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A **physical change** is a change in the state or properties of matter without any accompanying change in the chemical identities of the substances contained in the matter. Physical changes are observed when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water ([\[link\]](#)). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.



(a)



(b)

(a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water.  
(credit a: modification of work by

“95jb14”/Wikimedia Commons; credit  
b: modification of work by  
“mjneuby”/Flickr)

The change of one type of matter into another type (or the inability to change) is a **chemical property**. Examples of chemical properties include flammability, toxicity, acidity, and many other types of reactivity. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize ([link](#)). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



(a)



(b)

(a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by “Atoma”/Wikimedia Commons)

A **chemical change** always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of

chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting ([\[link\]](#)).



(a)



(b)



(c)



(d)

(a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide.

(b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor.

(c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change.

(d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form.

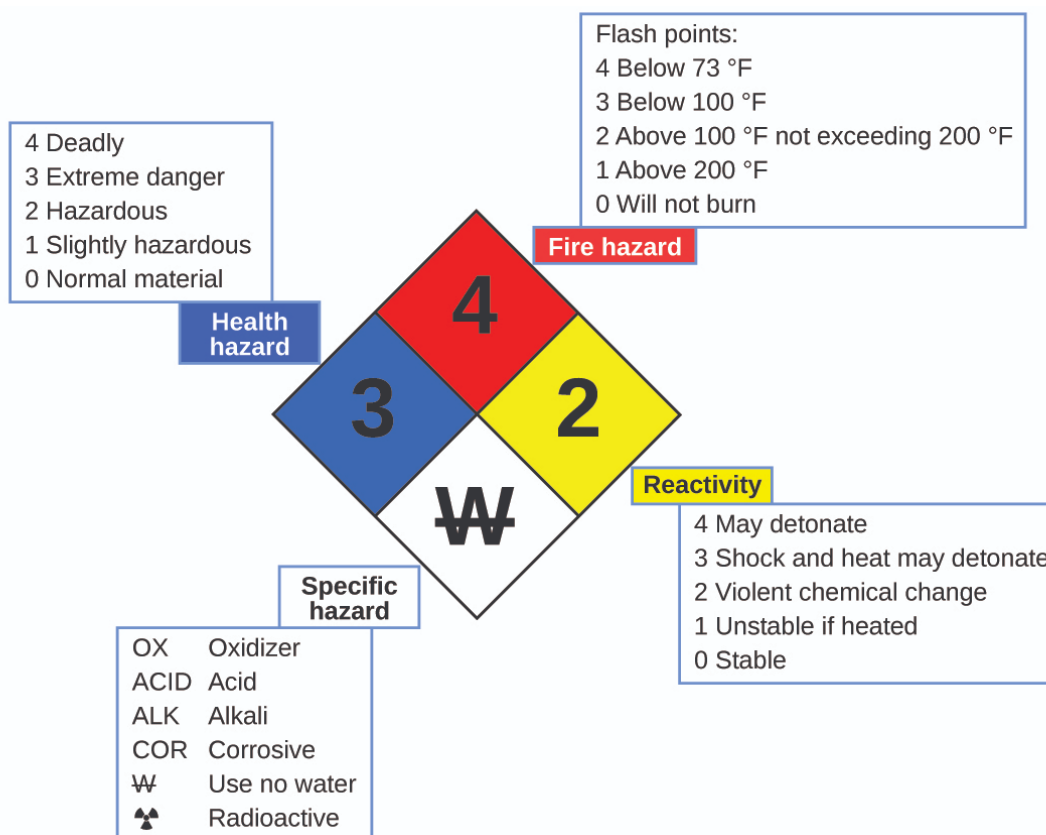
(credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an **extensive property**. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an **intensive property**. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

**Note:**

**Hazard Diamond**

You may have seen the symbol shown in [\[link\]](#) on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.



The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have intermediate conductivities).

The periodic table is a table of elements that places elements with similar properties close together ([link](#)). You will learn more about the periodic table as you continue your study of chemistry.

Period

Group

1

2

13

14

15

16

17

18

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The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

## Key Concepts and Summary

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such as flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Classify the six underlined properties in the following paragraph as chemical or physical:

Fluorine is a pale yellow gas that reacts with most substances. The free element melts at  $-220^{\circ}\text{C}$  and boils at  $-188^{\circ}\text{C}$ . Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

### Exercise:

#### Problem:

Classify each of the following changes as physical or chemical:

- (a) condensation of steam
  - (b) burning of gasoline
  - (c) souring of milk
  - (d) dissolving of sugar in water
  - (e) melting of gold
- 

**Solution:**

(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

**Exercise:**

**Problem:**

Classify each of the following changes as physical or chemical:

- (a) coal burning
- (b) ice melting
- (c) mixing chocolate syrup with milk
- (d) explosion of a firecracker
- (e) magnetizing of a screwdriver

**Exercise:**

**Problem:**

The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?

---

**Solution:**

physical

**Exercise:**



**Problem:**

A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?

**Exercise:****Problem:**

Explain the difference between extensive properties and intensive properties.

---

**Solution:**

The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

**Exercise:****Problem:**

Identify the following properties as either extensive or intensive.

- (a) volume
- (b) temperature
- (c) humidity
- (d) heat
- (e) boiling point

**Exercise:****Problem:**

The density ( $d$ ) of a substance is an intensive property that is defined as the ratio of its mass ( $m$ ) to its volume ( $V$ ).

**Equation:**

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad d = \frac{m}{V}$$

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

---

**Solution:**

Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect “cancel” this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

**Glossary**

chemical change

change producing a different kind of matter from the original kind of matter

chemical property

behavior that is related to the change of one kind of matter into another kind of matter

extensive property

property of a substance that depends on the amount of the substance

intensive property

property of a substance that is independent of the amount of the substance

physical change

change in the state or properties of matter that does not involve a change in its chemical composition

physical property

characteristic of matter that is not associated with any change in its chemical composition

## Measurements

By the end of this section, you will be able to:

- Explain the process of measurement
- Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide much of the information that informs the hypotheses, theories, and laws describing the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. (Scientific notation is also known as exponential notation; a review of this topic can be found in [Appendix B](#).) For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as  $2.98 \times 10^5$  kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as  $2.5 \times 10^{-6}$  kg.

**Units**, such as liters, pounds, and centimeters, are standards of comparison for measurements. A 2-liter bottle of a soft drink contains a volume of beverage that is twice that of the accepted volume of 1 liter. The meat used to prepare a 0.25-pound hamburger weighs one-fourth as much as the accepted weight of 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg

given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

The measurement units for seven fundamental properties (“base units”) are listed in [\[link\]](#). The standards for these units are fixed by international agreement, and they are called the **International System of Units** or **SI Units** (from the French, *Le Système International d’Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964. Units for other properties may be derived from these seven base units.

Base Units of the SI System		
Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Everyday measurement units are often defined as fractions or multiples of other units. Milk is commonly packaged in containers of 1 gallon (4 quarts), 1 quart (0.25 gallon), and one pint (0.5 quart). This same approach is used

with SI units, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means “one thousand,” which in scientific notation is  $10^3$  (1 kilometer = 1000 m =  $10^3$  m). The prefixes used and the powers to which 10 are raised are listed in [\[link\]](#).

Common Unit Prefixes			
Prefix	Symbol	Factor	Example
femto	f	$10^{-15}$	1 femtosecond (fs) = $1 \times 10^{-15}$ s (0.000000000000001 s)
pico	p	$10^{-12}$	1 picometer (pm) = $1 \times 10^{-12}$ m (0.000000000001 m)
nano	n	$10^{-9}$	4 nanograms (ng) = $4 \times 10^{-9}$ g (0.000000004 g)
micro	$\mu$	$10^{-6}$	1 microliter ( $\mu$ L) = $1 \times 10^{-6}$ L (0.000001 L)
milli	m	$10^{-3}$	2 millimoles (mmol) = $2 \times 10^{-3}$ mol (0.002 mol)
centi	c	$10^{-2}$	7 centimeters (cm) = $7 \times 10^{-2}$ m (0.07 m)
deci	d	$10^{-1}$	1 deciliter (dL) = $1 \times 10^{-1}$ L (0.1 L )

Common Unit Prefixes			
Prefix	Symbol	Factor	Example
kilo	k	$10^3$	1 kilometer (km) = $1 \times 10^3$ m (1000 m)
mega	M	$10^6$	3 megahertz (MHz) = $3 \times 10^6$ Hz (3,000,000 Hz)
giga	G	$10^9$	8 gigayears (Gyr) = $8 \times 10^9$ yr (8,000,000,000 yr)
tera	T	$10^{12}$	5 terawatts (TW) = $5 \times 10^{12}$ W (5,000,000,000,000 W)

**Note:**

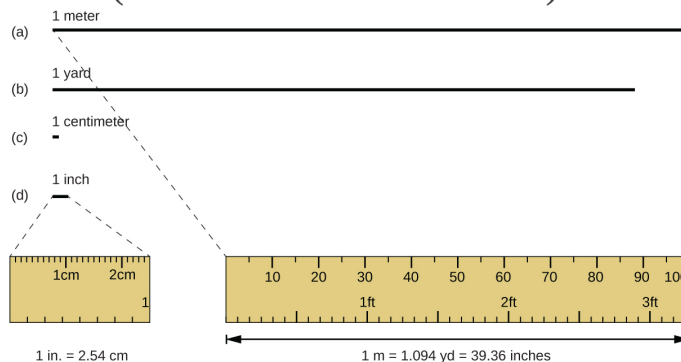
Need a refresher or more practice with scientific notation? Visit this [site](#) to go over the basics of scientific notation.

## SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

### Length

The standard unit of **length** in both the SI and original metric systems is the **meter (m)**. A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard ([\[link\]](#)); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers ( $1\text{ km} = 1000\text{ m} = 10^3\text{ m}$ ), whereas shorter distances can be reported in centimeters ( $1\text{ cm} = 0.01\text{ m} = 10^{-2}\text{ m}$ ) or millimeters ( $1\text{ mm} = 0.001\text{ m} = 10^{-3}\text{ m}$ ).



The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

## Mass

The standard unit of mass in the SI system is the **kilogram (kg)**. The kilogram was previously defined by the International Union of Pure and Applied Chemistry (IUPAC) as the mass of a specific reference object. This object was originally one liter of pure water, and more recently it was a metal cylinder made from a platinum-iridium alloy with a height and diameter of 39 mm ([\[link\]](#)). In May 2019, this definition was changed to one that is based instead on precisely measured values of several fundamental physical constants.[\[footnote\]](#) One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram ( $10^{-3}\text{ kg}$ ).



For details see <https://www.nist.gov/pml/weights-and-measures/si-units-mass>



This replica prototype kilogram as previously defined is housed at the National Institute of Standards and Technology (NIST) in Maryland.  
(credit: National Institutes of Standards and Technology)

## Temperature

Temperature is an intensive property. The SI unit of temperature is the **kelvin (K)**. The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°). The degree **Celsius (°C)** is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

## Time

The SI base unit of time is the **second (s)**. Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s =  $3 \times 10^{-6}$  and 5 megaseconds = 5,000,000 s =  $5 \times 10^6$  s. Alternatively, hours, days, and years can be used.

## Derived SI Units

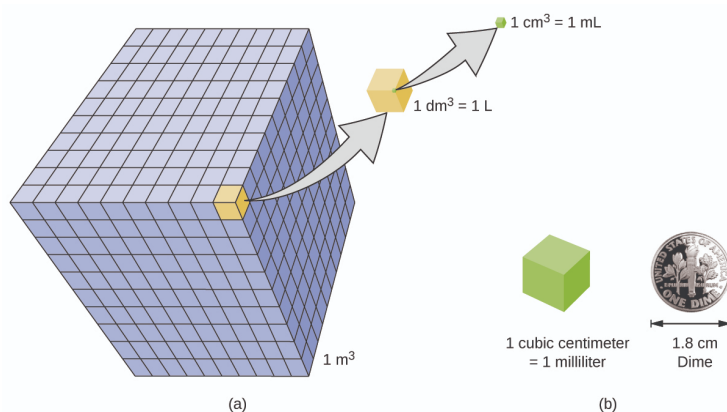
We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

## Volume

**Volume** is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length ([\[link\]](#)). The standard volume is a **cubic meter (m<sup>3</sup>)**, a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter ( $\text{dm}^3$ ). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

A **cubic centimeter ( $\text{cm}^3$ )** is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **cubic centimeter**) is often used by health professionals. A cubic centimeter is equivalent to a **milliliter (mL)** and is 1/1000 of a liter.



(a) The relative volumes are shown for cubes of  $1 \text{ m}^3$ ,  $1 \text{ dm}^3$  (1 L), and  $1 \text{ cm}^3$  (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a  $1\text{-cm}^3$  (1-mL) cube.

## Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The **density** of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter ( $\text{kg}/\text{m}^3$ ). For many situations, however, this is an inconvenient unit, and we often use grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ) for the densities of

solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm<sup>3</sup> (the density of gasoline) to 19 g/cm<sup>3</sup> (the density of gold). The density of air is about 1.2 g/L. [\[link\]](#) shows the densities of some common substances.

<b>Densities of Common Substances</b>		
<b>Solids</b>	<b>Liquids</b>	<b>Gases (at 25 °C and 1 atm)</b>
ice (at 0 °C) 0.92 g/cm <sup>3</sup>	water 1.0 g/cm <sup>3</sup>	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm <sup>3</sup>	ethanol 0.79 g/cm <sup>3</sup>	oxygen 1.31 g/L
iron 7.9 g/cm <sup>3</sup>	acetone 0.79 g/cm <sup>3</sup>	nitrogen 1.14 g/L
copper 9.0 g/cm <sup>3</sup>	glycerin 1.26 g/cm <sup>3</sup>	carbon dioxide 1.80 g/L
lead 11.3 g/cm <sup>3</sup>	olive oil 0.92 g/cm <sup>3</sup>	helium 0.16 g/L
silver 10.5 g/cm <sup>3</sup>	gasoline 0.70–0.77 g/cm <sup>3</sup>	neon 0.83 g/L
gold 19.3 g/cm <sup>3</sup>	mercury 13.6 g/cm <sup>3</sup>	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

**Equation:**

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

**Example:**

### **Calculation of Density**

Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold,  $19.3 \text{ g/cm}^3$ . What is the density of lead if a cube of lead has an edge length of  $2.00 \text{ cm}$  and a mass of  $90.7 \text{ g}$ ?

**Solution**

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

**Equation:**

$$\text{volume of lead cube} = 2.00 \text{ cm} \times 2.00 \text{ cm} \times 2.00 \text{ cm} = 8.00 \text{ cm}^3$$

**Equation:**

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7 \text{ g}}{8.00 \text{ cm}^3} = 11.3 \text{ g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

**Check Your Learning**

(a) To three decimal places, what is the volume of a cube ( $\text{cm}^3$ ) with an edge length of 0.843 cm?

(b) If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

**Note:**

**Answer:**

(a)  $0.599 \text{ cm}^3$ ; (b)  $8.91 \text{ g/cm}^3$

**Note:**

To learn more about the relationship between mass, volume, and density, use this [interactive simulator](#) to explore the density of different materials, like wood, ice, brick, and aluminum.

**Example:**

### Using Displacement of Water to Determine Density

This [PhET simulation](#) illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

### Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density =  $1.00 \text{ kg/L}$ ), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

**Equation:**

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{1.25 \text{ L}} = 4.00 \text{ kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

**Equation:**

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{10.00 \text{ L}} = 0.500 \text{ kg/L}$$

### Check Your Learning

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank.

Determine the density of the green block.

**Note:**

**Answer:**

2.00 kg/L

## Key Concepts and Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use SI (International System) units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and  $\text{g/cm}^3$  (for density). In many cases, it is convenient to use prefixes that yield fractional and multiple units, such as microseconds ( $10^{-6}$  seconds) and megahertz ( $10^6$  hertz), respectively.

## Key Equations

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

## Chemistry End of Chapter Exercises

### Exercise:

**Problem:** Is one liter about an ounce, a pint, a quart, or a gallon?

### Exercise:

**Problem:** Is a meter about an inch, a foot, a yard, or a mile?

---

### Solution:

about a yard

### Exercise:

### Problem:

Indicate the SI base units or derived units that are appropriate for the following measurements:

- (a) the length of a marathon race (26 miles 385 yards)
- (b) the mass of an automobile
- (c) the volume of a swimming pool
- (d) the speed of an airplane



- (e) the density of gold
- (f) the area of a football field
- (g) the maximum temperature at the South Pole on April 1, 1913

**Exercise:**

**Problem:**

Indicate the SI base units or derived units that are appropriate for the following measurements:

- (a) the mass of the moon
  - (b) the distance from Dallas to Oklahoma City
  - (c) the speed of sound
  - (d) the density of air
  - (e) the temperature at which alcohol boils
  - (f) the area of the state of Delaware
  - (g) the volume of a flu shot or a measles vaccination
- 

**Solution:**

(a) kilograms; (b) meters; (c) meters/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

**Exercise:**

**Problem:**

Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

- (a)  $10^3$

(b)  $10^{-2}$

(c) 0.1

(d)  $10^{-3}$

(e) 1,000,000

(f) 0.000001

**Exercise:**

**Problem:**

Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

(a) c

(b) d

(c) G

(d) k

(e) m

(f) n

(g) p

(h) T

---

**Solution:**

(a) centi-,  $\times 10^{-2}$ ; (b) deci-,  $\times 10^{-1}$ ; (c) Giga-,  $\times 10^9$ ; (d) kilo-,  $\times 10^3$ ;  
(e) milli-,  $\times 10^{-3}$ ; (f) nano-,  $\times 10^{-9}$ ; (g) pico-,  $\times 10^{-12}$ ; (h) tera-,  $\times 10^{12}$

**Exercise:**

**Problem:**

A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

- (a) Determine the density of this piece of jewelry.
- (b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

**Exercise:****Problem:**

Visit this [PhET density simulation](#) and select the Same Volume Blocks.

- (a) What are the mass, volume, and density of the yellow block?
- (b) What are the mass, volume and density of the red block?
- (c) List the block colors in order from smallest to largest mass.
- (d) List the block colors in order from lowest to highest density.
- (e) How are mass and density related for blocks of the same volume?

---

**Solution:**

(a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

**Exercise:****Problem:**

Visit this [PhET density simulation](#) and select Custom Blocks and then My Block.

(a) Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when  $\text{mass} < \text{volume}$ ?

(b) Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when  $\text{mass} > \text{volume}$ ?

(c) How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?

(d) How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

### **Exercise:**

#### **Problem:**

Visit this [PhET density simulation](#) and select Mystery Blocks.

(a) Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.

(b) Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.

(c) Order the Mystery Blocks from least dense to most dense. Explain.

---

#### **Solution:**

(a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L)

< D/red/ice (0.920 kg/L) < E/purple/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

## Glossary

Celsius (°C)

unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm<sup>3</sup> or cc)

volume of a cube with an edge length of exactly 1 cm

cubic meter (m<sup>3</sup>)

SI unit of volume

density

ratio of mass to volume for a substance or object

kelvin (K)

SI unit of temperature; 273.15 K = 0 °C

kilogram (kg)

standard SI unit of mass; 1 kg = approximately 2.2 pounds

length

measure of one dimension of an object

liter (L)

(also, cubic decimeter) unit of volume; 1 L = 1,000 cm<sup>3</sup>

meter (m)

standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)

1/1,000 of a liter; equal to 1 cm<sup>3</sup>

second (s)

SI unit of time

SI units (International System of Units)

standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit

standard of comparison for measurements

volume

amount of space occupied by an object

## Measurement Uncertainty, Accuracy, and Precision

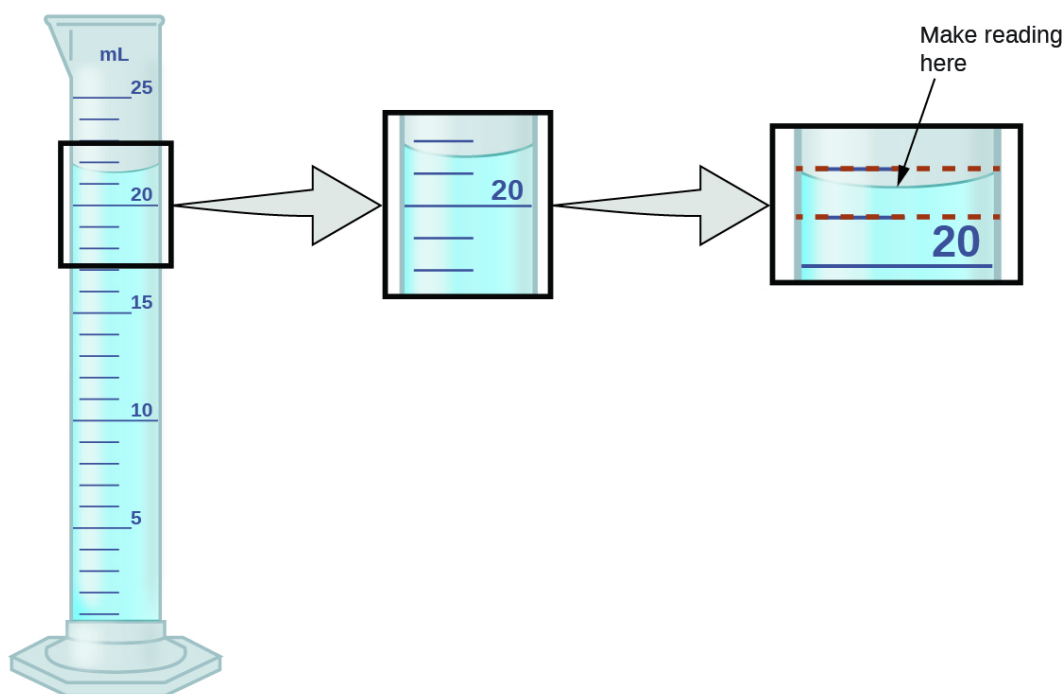
By the end of this section, you will be able to:

- Define accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an **exact number**. By counting the eggs in a carton, one can determine *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

## Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.



To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in [\[link\]](#). The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of  $\pm 0.01$  gram. If the coin is weighed on a more sensitive balance, the mass might be 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some **uncertainty**, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called **significant figures** or **significant digits**. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

A measurement result is properly reported when its significant digits accurately represent the certainty of the measurement process. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.



Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.



First nonzero figure on the left  
1267 m  
Four significant figures

First nonzero figure on the left  
55.0 g  
Three significant figures: note that the zero is to the right of the decimal point and therefore a significant figure

Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.

First nonzero figure on the left  
70.607 mL  
Five significant figures: all figures are measured including the two zeros

First nonzero figure on the left  
0.00832407 mL  
Six significant figures

The leading zeros in this example are not significant. We could use exponential notation (as described in [Appendix B](#)) and express the number as  $8.32407 \times 10^{-3}$ ; then the number 8.32407 contains all of the significant figures, and  $10^{-3}$  locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation:  $1.3 \times 10^3$  (two significant figures),  $1.30 \times 10^3$  (three significant figures, if the tens place was measured), or  $1.300 \times 10^3$  (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.

Significant figures: clearly result of measurement  
1300 g  
These zeros could be significant (measured), or they could be placeholders

When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely when evaluating whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as  $3.17 \times 10^8$  people.

## Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. Take the uncertainty in measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result

of a calculation with the correct number of significant figures, which is determined by the following three rules for **rounding** numbers:

1. When adding or subtracting numbers, round the result to the same number of decimal places as the number with the least number of decimal places (the least certain value in terms of addition and subtraction).
2. When multiplying or dividing numbers, round the result to the same number of digits as the number with the least number of significant figures (the least certain value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, “round down” and leave the retained digit unchanged; if it is more than or equal to 5, “round up” and increase the retained digit by 1.

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, is greater than or equal to 5)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, is greater than or equal to 5)
- 92.85 rounds “up” to 92.9 (the dropped digit is 5, is greater than or equal to 5)

Let’s work through these rules with a few examples.

**Example:**

**Rounding Numbers**

Round the following to the indicated number of significant figures:

- (a) 31.57 (to two significant figures)
- (b) 8.1649 (to three significant figures)
- (c) 0.051065 (to four significant figures)
- (d) 0.90275 (to four significant figures)

**Solution**

- (a) 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
- (b) 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is less than 5)
- (c) 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
- (d) 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

**Check Your Learning**

Round the following to the indicated number of significant figures:

- (a) 0.424 (to two significant figures)
- (b) 0.0038661 (to three significant figures)
- (c) 421.25 (to four significant figures)
- (d) 28,683.5 (to five significant figures)

**Note:**

**Answer:**

- (a) 0.42; (b) 0.00387; (c) 421.3; (d) 28,684

**Example:****Addition and Subtraction with Significant Figures**

Rule: When adding or subtracting numbers, round the result to the same number of decimal places as the number with the fewest decimal places (i.e., the least certain value in terms of addition and subtraction).

(a) Add 1.0023 g and 4.383 g.

(b) Subtract 421.23 g from 486 g.

**Solution**

(a)

$$\begin{array}{r} 1.0023 \text{ g} \\ + 4.383 \text{ g} \\ \hline 5.3853 \text{ g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{r} 486 \text{ g} \\ - 421.23 \text{ g} \\ \hline 64.77 \text{ g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)

1.0023 ← Ten thousandths place  
+ 4.383 ← Thousandths place: least precise  
5.3853  
↑  
Round to thousandths  
(a)

486 g  
- 421.23 g  
64.77 g  
↑  
Round to ones  
(b) → Answer is 65 g

**Check Your Learning**

(a) Add 2.334 mL and 0.31 mL.

(b) Subtract 55.8752 m from 56.533 m.

**Note:****Answer:**

(a) 2.64 mL; (b) 0.658 m

**Example:****Multiplication and Division with Significant Figures**

Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain value in terms of multiplication and

division).

(a) Multiply 0.6238 cm by 6.6 cm.

(b) Divide 421.23 g by 486 mL.

**Solution**

(a)

$0.6238 \text{ cm} \times 6.6 \text{ cm} = 4.11708 \text{ cm}^2 \rightarrow$  result is  $4.1 \text{ cm}^2$  (round to two significant figures)

four significant figures  $\times$  two significant figures  $\rightarrow$  two significant figures answer

(b)

$\frac{421.23 \text{ g}}{486 \text{ mL}} = 0.86728... \text{ g/mL} \rightarrow$  result is  $0.867 \text{ g/mL}$  (round to three significant figures)

$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow$  three significant figures answer

**Check Your Learning**

(a) Multiply 2.334 cm and 0.320 cm.

(b) Divide 55.8752 m by 56.53 s.

**Note:**

**Answer:**

(a)  $0.747 \text{ cm}^2$  (b)  $0.9884 \text{ m/s}$

In the midst of all these technicalities, it is important to keep in mind the reason for these rules about significant figures and rounding—to correctly represent the certainty of the values reported and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

**Example:**

**Calculation with Significant Figures**

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

**Solution**

**Equation:**

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44 \text{ dm} \times 5.920 \text{ dm} \times 2.54 \text{ dm} \\ &= 202.09459... \text{ dm}^3 \text{ (value from calculator)} \\ &= 202 \text{ dm}^3, \text{ or } 202 \text{ L (answer rounded to three significant figures)} \end{aligned}$$

**Check Your Learning**

What is the density of a liquid with a mass of 31.1415 g and a volume of  $30.13 \text{ cm}^3$ ?

**Note:**

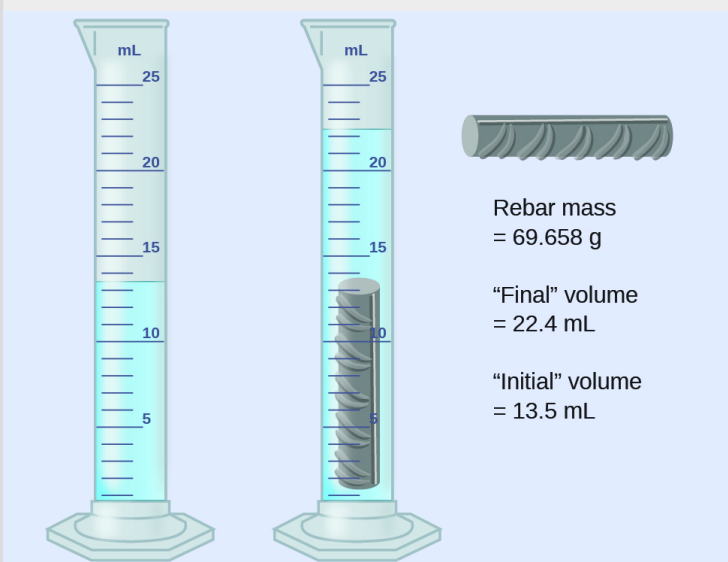
**Answer:**

1.034 g/mL

**Example:**

**Experimental Determination of Density Using Water Displacement**

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



(a) Use these values to determine the density of this piece of rebar.

(b) Rebar is mostly iron. Does your result in (a) support this statement? How?

**Solution**

The volume of the piece of rebar is equal to the volume of the water displaced:

**Equation:**

$$\text{volume} = 22.4 \text{ mL} - 13.5 \text{ mL} = 8.9 \text{ mL} = 8.9 \text{ cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

**Equation:**

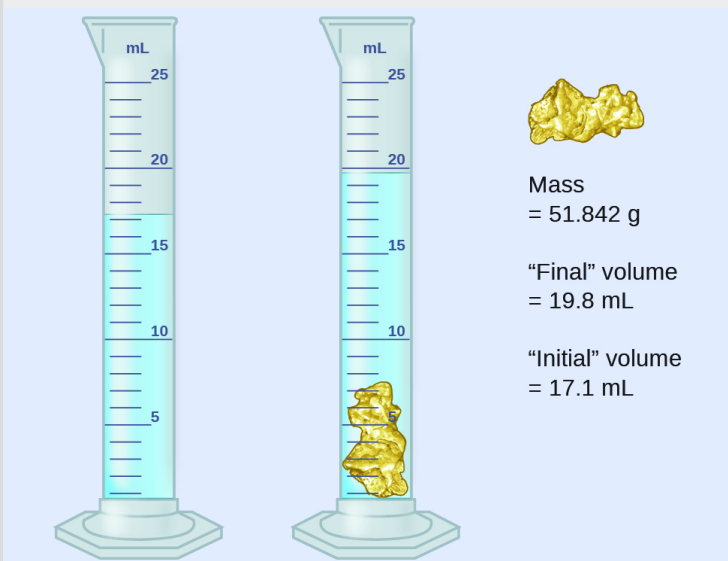
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658 \text{ g}}{8.9 \text{ cm}^3} = 7.8 \text{ g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)

From [\[link\]](#), the density of iron is 7.9 g/cm<sup>3</sup>, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

**Check Your Learning**

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.



- (a) Use these values to determine the density of this material.  
(b) Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

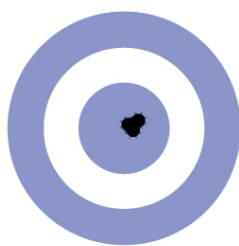
**Note:**

**Answer:**

(a)  $19 \text{ g/cm}^3$ ; (b) It is likely gold; the right appearance for gold and very close to the density given for gold in [\[link\]](#).

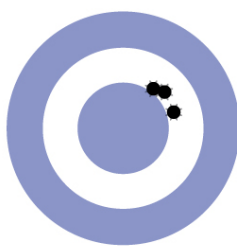
## Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to evaluate both the **precision** and the **accuracy** of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition ([\[link\]](#)).



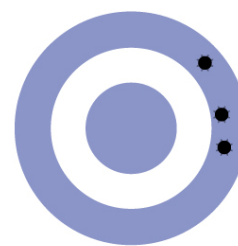
Accurate  
and precise

(a)



Precise,  
not accurate

(b)



Not accurate,  
not precise

(c)

(a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in [\[link\]](#).

Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers		
Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup

both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

## Key Concepts and Summary

Quantities can be defined or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the quantity's number. The uncertainty of a calculated quantity depends on the uncertainties in the quantities used in the calculation and is reflected in how the value is rounded. Quantities are characterized with regard to accuracy (closeness to a true or accepted value) and precision (variation among replicate measurement results).

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Express each of the following numbers in scientific notation with correct significant figures:

- (a) 711.0
- (b) 0.239
- (c) 90743
- (d) 134.2
- (e) 0.05499
- (f) 10000.0
- (g) 0.000000738592

### Exercise:

#### Problem:

Express each of the following numbers in exponential notation with correct significant figures:

- (a) 704
- (b) 0.03344
- (c) 547.9
- (d) 22086
- (e) 1000.00
- (f) 0.0000000651



(g) 0.007157

---

**Solution:**

(a)  $7.04 \times 10^2$ ; (b)  $3.344 \times 10^{-2}$ ; (c)  $5.479 \times 10^2$ ; (d)  $2.2086 \times 10^4$ ; (e)  $1.00000 \times 10^3$ ; (f)  $6.51 \times 10^{-8}$ ; (g)  $7.157 \times 10^{-3}$

**Exercise:**

**Problem:**

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

- (a) the number of eggs in a basket
- (b) the mass of a dozen eggs
- (c) the number of gallons of gasoline necessary to fill an automobile gas tank
- (d) the number of cm in 2 m
- (e) the mass of a textbook
- (f) the time required to drive from San Francisco to Kansas City at an average speed of 53 mi/h

**Exercise:**

**Problem:**

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

- (a) the number of seconds in an hour
- (b) the number of pages in this book
- (c) the number of grams in your weight
- (d) the number of grams in 3 kilograms
- (e) the volume of water you drink in one day
- (f) the distance from San Francisco to Kansas City

---

**Solution:**

(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

**Exercise:**

**Problem:** How many significant figures are contained in each of the following measurements?

- (a) 38.7 g
- (b)  $2 \times 10^{18}$  m
- (c) 3,486,002 kg
- (d)  $9.74150 \times 10^{-4}$  J
- (e)  $0.0613 \text{ cm}^3$
- (f) 17.0 kg
- (g) 0.01400 g/mL

**Exercise:**

**Problem:** How many significant figures are contained in each of the following measurements?

- (a) 53 cm
- (b)  $2.05 \times 10^8$  m
- (c) 86,002 J
- (d)  $9.740 \times 10^4$  m/s
- (e)  $10.0613 \text{ m}^3$
- (f) 0.17 g/mL
- (g) 0.88400 s

---

**Solution:**

(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

**Exercise:**

**Problem:**

The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.

- (a) 0.0055 g active ingredients
- (b) 12 tablets
- (c) 3% hydrogen peroxide
- (d) 5.5 ounces
- (e) 473 mL

- (f) 1.75% bismuth
- (g) 0.001% phosphoric acid
- (h) 99.80% inert ingredients

**Exercise:**

**Problem:** Round off each of the following numbers to two significant figures:

- (a) 0.436
  - (b) 9.000
  - (c) 27.2
  - (d) 135
  - (e)  $1.497 \times 10^{-3}$
  - (f) 0.445
- 

**Solution:**

(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e)  $1.5 \times 10^{-3}$ ; (f) 0.45

**Exercise:**

**Problem:** Round off each of the following numbers to two significant figures:

- (a) 517
- (b) 86.3
- (c)  $6.382 \times 10^3$
- (d) 5.0008
- (e) 22.497
- (f) 0.885

**Exercise:**

**Problem:**

Perform the following calculations and report each answer with the correct number of significant figures.

- (a)  $628 \times 342$
- (b)  $(5.63 \times 10^2) \times (7.4 \times 10^3)$

(c)  $\frac{28.0}{13.483}$

(d)  $8119 \times 0.000023$

(e)  $14.98 + 27,340 + 84.7593$

(f)  $42.7 + 0.259$

---

**Solution:**

(a)  $2.15 \times 10^5$ ; (b)  $4.2 \times 10^6$ ; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

**Exercise:**

**Problem:**

Perform the following calculations and report each answer with the correct number of significant figures.

(a)  $62.8 \times 34$

(b)  $0.147 + 0.0066 + 0.012$

(c)  $38 \times 95 \times 1.792$

(d)  $15 - 0.15 - 0.6155$

(e)  $8.78 \times \left( \frac{0.0500}{0.478} \right)$

(f)  $140 + 7.68 + 0.014$

(g)  $28.7 - 0.0483$

(h)  $\frac{(88.5 - 87.57)}{45.13}$

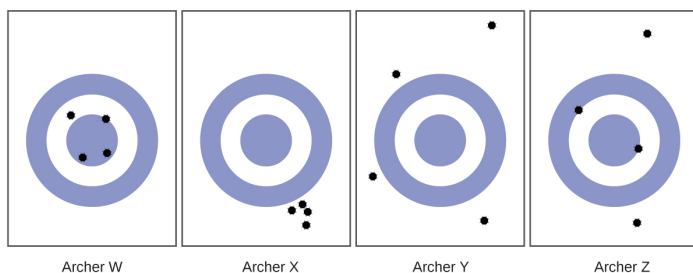
**Exercise:**

**Problem:** Consider the results of the archery contest shown in this figure.

(a) Which archer is most precise?

(b) Which archer is most accurate?

(c) Who is both least precise and least accurate?



### Solution:

(a) Archer X; (b) Archer W; (c) Archer Y

### Exercise:

**Problem:** Classify the following sets of measurements as accurate, precise, both, or neither.

(a) Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g

(b) Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL

(c) Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%

### Glossary

accuracy

how closely a measurement aligns with a correct value

exact number

number derived by counting or by definition

precision

how closely a measurement matches the same measurement when repeated

rounding

procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

significant figures

(also, significant digits) all of the measured digits in a determination, including the uncertain last digit

uncertainty

estimate of amount by which measurement differs from true value

## Mathematical Treatment of Measurement Results

By the end of this section, you will be able to:

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities
- Use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

**Equation:**

$$\text{speed} = \frac{\text{distance}}{\text{time}}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

**Equation:**

$$\frac{100 \text{ m}}{10 \text{ s}} = 10 \text{ m/s}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity ( $100/10 = 10$ ) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity ( $\text{m/s} = \text{m/s}$ ). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation among the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

**Equation:**

$$\text{time} = \frac{\text{distance}}{\text{speed}}$$

The time can then be computed as:

**Equation:**

$$\frac{25 \text{ m}}{10 \text{ m/s}} = 2.5 \text{ s}$$

Again, arithmetic on the numbers ( $25/10 = 2.5$ ) was accompanied by the same arithmetic on the units ( $\text{m/m/s} = \text{s}$ ) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is “1”—or, as commonly phrased, the units “cancel.”

These calculations are examples of a versatile mathematical approach known as **dimensional analysis** (or the **factor-label method**). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

## Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a **unit conversion factor**. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

**Equation:**

$$\frac{2.54 \text{ cm}}{1 \text{ in.}} (2.54 \text{ cm} = 1 \text{ in.}) \text{ or } 2.54 \frac{\text{cm}}{\text{in.}}$$

Several other commonly used conversion factors are given in [\[link\]](#).

Common Conversion Factors		
Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft <sup>3</sup> = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

When a quantity (such as distance in inches) is multiplied by an appropriate unit conversion factor, the quantity is converted to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

**Equation:**

$$34 \cancel{\text{in.}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{in.}}} = 86 \text{ cm}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield  $\frac{\text{in.} \times \text{cm}}{\text{in.}}$ . Just as for numbers, a ratio of identical units is also numerically equal to one,  $\frac{\text{in.}}{\text{in.}} = 1$ , and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to “cancel.”) Dimensional analysis may be used to confirm the proper application of unit conversion factors as demonstrated in the following example.

**Example:**

**Using a Unit Conversion Factor**

The mass of a competition frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g ([\[link\]](#)).

**Solution**

Given the conversion factor, the mass in ounces may be derived using an equation similar to the one used for converting length from inches to centimeters.

**Equation:**

$$x \text{ oz} = 125 \text{ g} \times \text{unit conversion factor}$$

The unit conversion factor may be represented as:

**Equation:**

$$\frac{1 \text{ oz}}{28.349 \text{ g}} \text{ and } \frac{28.349 \text{ g}}{1 \text{ oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

**Equation:**

$$\begin{aligned} x \text{ oz} &= 125 \cancel{\text{ g}} \times \frac{1 \text{ oz}}{28.349 \cancel{\text{ g}}} \\ &= \left( \frac{125}{28.349} \right) \text{ oz} \\ &= 4.41 \text{ oz (three significant figures)} \end{aligned}$$

### Check Your Learning

Convert a volume of 9.345 qt to liters.

**Note:**

**Answer:**

8.844 L

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to ensure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

### Example:

#### Computing Quantities from Measurement Results and Known Mathematical Relations

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

#### Solution

Since density =  $\frac{\text{mass}}{\text{volume}}$ , we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A  $\times$  unit conversion factor. The necessary conversion factors are given in [\[link\]](#): 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. Mass may be converted from pounds to grams as follows:

**Equation:**

$$9.26 \cancel{\text{ lb}} \times \frac{453.59 \text{ g}}{1 \cancel{\text{ lb}}} = 4.20 \times 10^3 \text{ g}$$

Volume may be converted from quarts to milliliters via two steps:

Convert quarts to  
liters. **Equation:**

$$4.00 \cancel{\text{ qt}} \times \frac{1 \text{ L}}{1.0567 \cancel{\text{ qt}}} = 3.78 \text{ L}$$

Convert liters to  
milliliters. **Equation:**



$$3.78 \cancel{\text{ L}} \times \frac{1000 \text{ mL}}{1 \cancel{\text{ L}}} = 3.78 \times 10^3 \text{ mL}$$

Then,

**Equation:**

$$\text{density} = \frac{4.20 \times 10^3 \text{ g}}{3.78 \times 10^3 \text{ mL}} = 1.11 \text{ g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

**Equation:**

$$\frac{9.26 \cancel{\text{ L}}}{4.00 \cancel{\text{ qt}}} \times \frac{453.59 \text{ g}}{1 \cancel{\text{ lb}}} \times \frac{1.0567 \cancel{\text{ qt}}}{1 \cancel{\text{ L}}} \times \frac{1 \cancel{\text{ L}}}{1000 \text{ mL}} = 1.11 \text{ g/mL}$$

### Check Your Learning

What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

**Note:**

**Answer:**

$$2.956 \times 10^{-2} \text{ L}$$

### Example:

#### Computing Quantities from Measurement Results and Known Mathematical Relations

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

(a) What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?

(b) If gasoline costs \$3.80 per gallon, what was the fuel cost for this trip?

**Solution**

(a) First convert distance from kilometers to miles:

**Equation:**

$$1250 \cancel{\text{ km}} \times \frac{0.62137 \text{ mi}}{1 \cancel{\text{ km}}} = 777 \text{ mi}$$

and then convert volume from liters to gallons:

**Equation:**

$$213 \cancel{\text{ L}} \times \frac{1.0567 \cancel{\text{ qt}}}{1 \cancel{\text{ L}}} \times \frac{1 \text{ gal}}{4 \cancel{\text{ qt}}} = 56.3 \text{ gal}$$

Finally,

**Equation:**

$$(\text{average}) \text{ mileage} = \frac{777 \text{ mi}}{56.3 \text{ gal}} = 13.8 \text{ miles/gallon} = 13.8 \text{ mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

**Equation:**

$$\frac{1250 \cancel{\text{km}}}{213 \cancel{\text{L}}} \times \frac{0.62137 \text{ mi}}{1 \cancel{\text{km}}} \times \frac{1 \cancel{\text{L}}}{1.0567 \cancel{\text{qt}}} \times \frac{4 \cancel{\text{qt}}}{1 \text{ gal}} = 13.8 \text{ mpg}$$

(b) Using the previously calculated volume in gallons, we find:

**Equation:**

$$56.3 \cancel{\text{gal}} \times \frac{\$3.80}{1 \cancel{\text{gal}}} = \$214$$

### Check Your Learning

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

(a) What (average) fuel economy, in miles per gallon, did the Prius get during this trip?

(b) If gasoline costs \$3.90 per gallon, what was the fuel cost for this trip?

**Note:**

**Answer:**

(a) 51 mpg; (b) \$62

## Conversion of Temperature Units

We use the word **temperature** to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes, and the position of the trapped liquid along a printed scale may be used as a measure of temperature.

Temperature scales are defined relative to selected reference temperatures: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the **Fahrenheit** scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another ( $y = mx$ ). Using familiar length units as one example:

**Equation:**

$$\text{length in feet} = \left( \frac{1 \text{ ft}}{12 \text{ in.}} \right) \times \text{length in inches}$$

where  $y$  = length in feet,  $x$  = length in inches, and the proportionality constant,  $m$ , is the conversion factor. The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one ( $y = mx + b$ ). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor,  $m$ , it also must take into account differences in the scales' zero points ( $b$ ).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as  $x$  and the Fahrenheit temperature as  $y$ , the slope,  $m$ , is computed to be:

**Equation:**

$$m = \frac{\Delta y}{\Delta x} = \frac{212\text{ }^{\circ}\text{F} - 32\text{ }^{\circ}\text{F}}{100\text{ }^{\circ}\text{C} - 0\text{ }^{\circ}\text{C}} = \frac{180\text{ }^{\circ}\text{F}}{100\text{ }^{\circ}\text{C}} = \frac{9\text{ }^{\circ}\text{F}}{5\text{ }^{\circ}\text{C}}$$

The y-intercept of the equation,  $b$ , is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

**Equation:**

$$b = y - mx = 32\text{ }^{\circ}\text{F} - \frac{9\text{ }^{\circ}\text{F}}{5\text{ }^{\circ}\text{C}} \times 0\text{ }^{\circ}\text{C} = 32\text{ }^{\circ}\text{F}$$

The equation relating the temperature ( $T$ ) scales is then:

**Equation:**

$$T_{\text{F}} = \left( \frac{9\text{ }^{\circ}\text{F}}{5\text{ }^{\circ}\text{C}} \times T_{\text{C}} \right) + 32\text{ }^{\circ}\text{F}$$

An abbreviated form of this equation that omits the measurement units is:

**Equation:**

$$T_{\text{F}} = \left( \frac{9}{5} \times T_{\text{C}} \right) + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

**Equation:**

$$T_{\text{C}} = \frac{5}{9}(T_{\text{F}} - 32)$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. Since the kelvin temperature scale is absolute, a degree symbol is not included in the unit abbreviation, K. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at  $-273.15\text{ }^{\circ}\text{C}$ . In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin, proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature is 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of  $1\text{ } \frac{\text{K}}{^{\circ}\text{C}}$ . Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

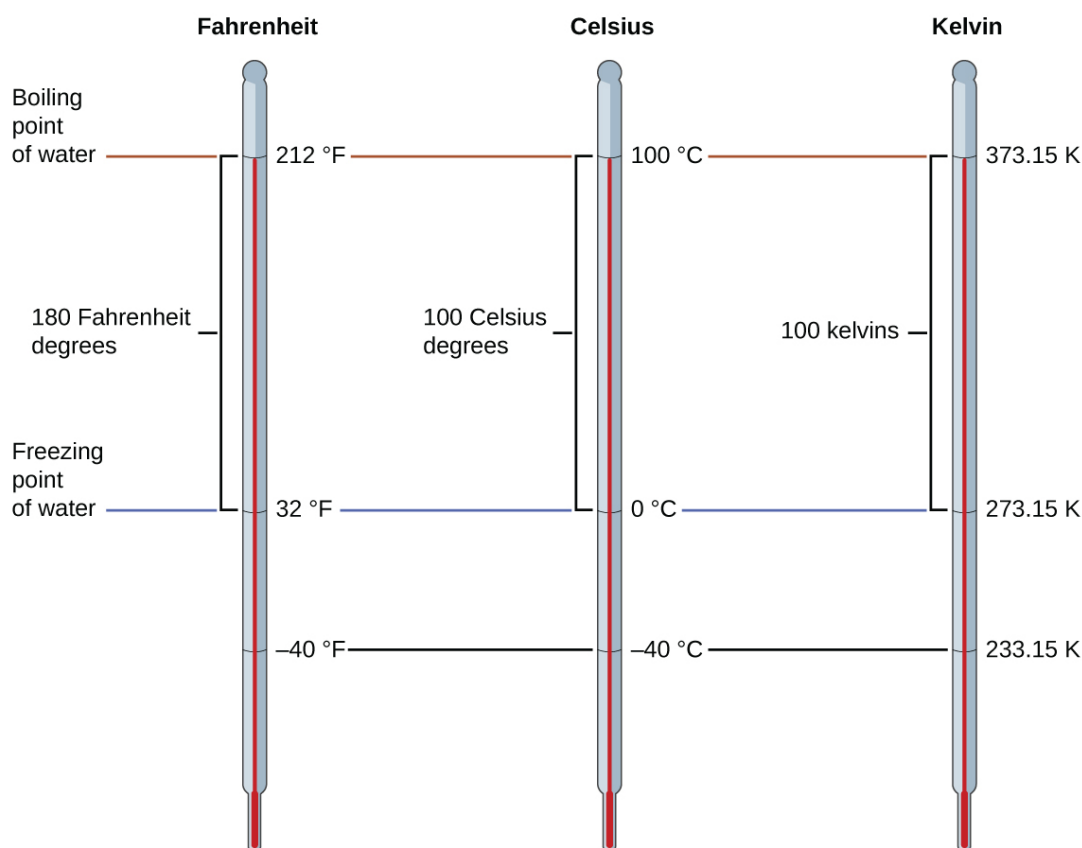
**Equation:**

$$T_{\text{K}} = T_{\text{C}} + 273.15$$

**Equation:**

$$T_{\text{C}} = T_{\text{K}} - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. [\[link\]](#) shows the relationship among the three temperature scales.



The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

**Example:**

**Conversion from Celsius**

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on the Fahrenheit scale?

**Solution**

**Equation:**

$$K = ^\circ C + 273.15 = 37.0 + 273.2 = 310.2 \text{ K}$$

**Equation:**

$$^{\circ}\text{F} = \frac{9}{5}^{\circ}\text{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6^{\circ}\text{F}$$

### Check Your Learning

Convert 80.92 °C to K and °F.

**Note:**

**Answer:**

354.07 K, 177.7 °F

### Example:

#### Conversion from Fahrenheit

Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?

**Solution**

**Equation:**

$$^{\circ}\text{C} = \frac{5}{9}(^{\circ}\text{F} - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232^{\circ}\text{C} \longrightarrow \text{set oven to } 230^{\circ}\text{C} \quad (\text{two significant figures})$$

**Equation:**

$$\text{K} = ^{\circ}\text{C} + 273.15 = 230 + 273 = 503 \text{ K} \longrightarrow 5.0 \times 10^2\text{K} \quad (\text{two significant figures})$$

### Check Your Learning

Convert 50 °F to °C and K.

**Note:**

**Answer:**

10 °C, 280 K

## Key Concepts and Summary

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

## Key Equations

$$T_{\text{C}} = \frac{5}{9} \times (T_{\text{F}} - 32)$$

$$T_{\text{F}} = \left( \frac{9}{5} \times T_{\text{C}} \right) + 32$$

$$T_{\text{K}} = ^{\circ}\text{C} + 273.15$$

$$T_{\text{C}} = \text{K} - 273.15$$

## Chemistry End of Chapter Exercises

### Exercise:

**Problem:** Write conversion factors (as ratios) for the number of:

- (a) yards in 1 meter
- (b) liters in 1 liquid quart
- (c) pounds in 1 kilogram

### Solution:

(a)  $\frac{1.0936 \text{ yd}}{1 \text{ m}}$ ; (b)  $\frac{0.94635 \text{ L}}{1 \text{ qt}}$ ; (c)  $\frac{2.2046 \text{ lb}}{1 \text{ kg}}$

### Exercise:

**Problem:** Write conversion factors (as ratios) for the number of:

- (a) kilometers in 1 mile
- (b) liters in 1 cubic foot
- (c) grams in 1 ounce

### Exercise:

#### Problem:

The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

#### Solution:

$$\frac{2.0 \text{ L}}{67.6 \text{ fl oz}} = \frac{0.030 \text{ L}}{1 \text{ fl oz}}$$

Only two significant figures are justified.

### Exercise:

#### Problem:

The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

### Exercise:

**Problem:**

Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

---

**Solution:**

68–71 cm; 400–450 g

**Exercise:****Problem:**

A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimeters and grams?

**Exercise:**

**Problem:** How many milliliters of a soft drink are contained in a 12.0-oz can?

---

**Solution:**

355 mL

**Exercise:**

**Problem:** A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?

**Exercise:**

**Problem:** The diameter of a red blood cell is about  $3 \times 10^{-4}$  in. What is its diameter in centimeters?

---

**Solution:**

$8 \times 10^{-4}$  cm

**Exercise:****Problem:**

The distance between the centers of the two oxygen atoms in an oxygen molecule is  $1.21 \times 10^{-8}$  cm. What is this distance in inches?

**Exercise:**

**Problem:** Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?

---

**Solution:**

yes; weight = 89.4 kg

**Exercise:****Problem:**

A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?

**Exercise:**

**Problem:** Many medical laboratory tests are run using 5.0  $\mu$ L blood serum. What is this volume in milliliters?

---

**Solution:**

$$5.0 \times 10^{-3} \text{ mL}$$

**Exercise:**

**Problem:** If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?

**Exercise:**

**Problem:**

Use scientific (exponential) notation to express the following quantities in terms of the SI base units in [\[link\]](#):

(a) 0.13 g

(b) 232 Gg

(c) 5.23 pm

(d) 86.3 mg

(e) 37.6 cm

(f) 54  $\mu\text{m}$

(g) 1 Ts

(h) 27 ps

(i) 0.15 mK

---

**Solution:**

(a)  $1.3 \times 10^{-4} \text{ kg}$ ; (b)  $2.32 \times 10^8 \text{ kg}$ ; (c)  $5.23 \times 10^{-12} \text{ m}$ ; (d)  $8.63 \times 10^{-5} \text{ kg}$ ; (e)  $3.76 \times 10^{-1} \text{ m}$ ; (f)  $5.4 \times 10^{-5} \text{ m}$ ; (g)  $1 \times 10^{12} \text{ s}$ ; (h)  $2.7 \times 10^{-11} \text{ s}$ ; (i)  $1.5 \times 10^{-4} \text{ K}$

**Exercise:**

**Problem:** Complete the following conversions between SI units.

(a) 612 g = \_\_\_\_\_ mg

(b) 8.160 m = \_\_\_\_\_ cm

(c) 3779  $\mu\text{g}$  = \_\_\_\_\_ g

(d) 781 mL = \_\_\_\_\_ L

(e) 4.18 kg = \_\_\_\_\_ g

(f) 27.8 m = \_\_\_\_\_ km

(g) 0.13 mL = \_\_\_\_\_ L

(h) 1738 km = \_\_\_\_\_ m

(i) 1.9 Gg = \_\_\_\_\_ g

**Exercise:**



**Problem:**

Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?

---

**Solution:**

45.4 L

**Exercise:**

**Problem:** Milk is sold by the liter in many countries. What is the volume of exactly 1/2 gal of milk in liters?

**Exercise:**

**Problem:** A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

---

**Solution:**

$1.0160 \times 10^3$  kg

**Exercise:**

**Problem:** Make the conversion indicated in each of the following:

- (a) the men's world record long jump, 29 ft 4¼ in., to meters
- (b) the greatest depth of the ocean, about 6.5 mi, to kilometers
- (c) the area of the state of Oregon, 96,981 mi<sup>2</sup>, to square kilometers
- (d) the volume of 1 gill (exactly 4 oz) to milliliters
- (e) the estimated volume of the oceans, 330,000,000 mi<sup>3</sup>, to cubic kilometers.
- (f) the mass of a 3525-lb car to kilograms
- (g) the mass of a 2.3-oz egg to grams

**Exercise:**

**Problem:** Make the conversion indicated in each of the following:

- (a) the length of a soccer field, 120 m (three significant figures), to feet
  - (b) the height of Mt. Kilimanjaro, at 19,565 ft, the highest mountain in Africa, to kilometers
  - (c) the area of an 8.5- × 11-inch sheet of paper in cm<sup>2</sup>
  - (d) the displacement volume of an automobile engine, 161 in.<sup>3</sup>, to liters
  - (e) the estimated mass of the atmosphere,  $5.6 \times 10^{15}$  tons, to kilograms
  - (f) the mass of a bushel of rye, 32.0 lb, to kilograms
  - (g) the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)
- 

**Solution:**

(a) 394 ft; (b) 5.9634 km; (c)  $6.0 \times 10^2$ ; (d) 2.64 L; (e)  $5.1 \times 10^{18}$  kg; (f) 14.5 kg; (g) 324 mg

**Exercise:****Problem:**

Many chemistry conferences have held a 50-Trillion Angstrom Run (two significant figures). How long is this run in kilometers and in miles? ( $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ )

**Exercise:****Problem:**

A chemist's 50-Trillion Angstrom Run (see [\[link\]](#)) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? ( $1 \text{ \AA} = 1 \times 10^{-8} \text{ cm}$ )

---

**Solution:**

0.46 m; 1.5 ft/cubit

**Exercise:****Problem:**

The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms and pounds of the fuel in a full tank.

**Exercise:****Problem:**

As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

---

**Solution:**

Yes, the acid's volume is 123 mL.

**Exercise:****Problem:**

To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?

**Exercise:****Problem:**

A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

---

**Solution:**

62.6 in (about 5 ft 3 in.) and 101 lb

**Exercise:****Problem:**

In a recent Grand Prix, the winner completed the race with an average speed of 229.8 km/h. What was his speed in miles per hour, meters per second, and feet per second?

**Exercise:**

**Problem:** Solve these problems about lumber dimensions.

(a) To describe to a European how houses are constructed in the US, the dimensions of “two-by-four” lumber must be converted into metric units. The thickness  $\times$  width  $\times$  length dimensions are 1.50 in.  $\times$  3.50 in.  $\times$  8.00 ft in the US. What are the dimensions in cm  $\times$  cm  $\times$  m?

(b) This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimeters?

---

**Solution:**

(a) 3.81 cm  $\times$  8.89 cm  $\times$  2.44 m; (b) 40.6 cm

**Exercise:**

**Problem:**

The mercury content of a stream was believed to be above the minimum considered safe—1 part per billion (ppb) by weight. An analysis indicated that the concentration was 0.68 parts per billion. What quantity of mercury in grams was present in 15.0 L of the water, the density of which is 0.998 g/ml?

$$(1 \text{ ppb Hg} = \frac{1 \text{ ng Hg}}{1 \text{ g water}})$$

**Exercise:**

**Problem:** Calculate the density of aluminum if 27.6 cm<sup>3</sup> has a mass of 74.6 g.

---

**Solution:**

$$2.70 \text{ g/cm}^3$$

**Exercise:**

**Problem:**

Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm<sup>3</sup>?

**Exercise:**

**Problem:** Calculate these masses.

(a) What is the mass of 6.00 cm<sup>3</sup> of mercury, density = 13.5939 g/cm<sup>3</sup>?

(b) What is the mass of 25.0 mL octane, density = 0.702 g/cm<sup>3</sup>?

---

**Solution:**

(a) 81.6 g; (b) 17.6 g

**Exercise:**

**Problem:** Calculate these masses.

(a) What is the mass of 4.00 cm<sup>3</sup> of sodium, density = 0.97 g/cm<sup>3</sup>?

(b) What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

**Exercise:**

**Problem:** Calculate these volumes.

(a) What is the volume of 25 g iodine, density = 4.93 g/cm<sup>3</sup>?

(b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

---

**Solution:**

(a) 5.1 mL; (b) 37 L

**Exercise:**

**Problem:** Calculate these volumes.

(a) What is the volume of 11.3 g graphite, density = 2.25 g/cm<sup>3</sup>?

(b) What is the volume of 39.657 g bromine, density = 2.928 g/cm<sup>3</sup>?

**Exercise:**

**Problem:** Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.

---

**Solution:**

5371 °F, 3239 K

**Exercise:**

**Problem:** Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.

**Exercise:**

**Problem:** Convert the temperature of the coldest area in a freezer, -10 °F, to degrees Celsius and kelvin.

---

**Solution:**

-23 °C, 250 K

**Exercise:**

**Problem:** Convert the temperature of dry ice, -77 °C, into degrees Fahrenheit and kelvin.

**Exercise:**

**Problem:** Convert the boiling temperature of liquid ammonia, -28.1 °F, into degrees Celsius and kelvin.

---

**Solution:**

-33.4 °C, 239.8 K

**Exercise:**

**Problem:**

The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?

**Exercise:**

**Problem:**

The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?

---

**Solution:**

113 °F

## **Glossary**

dimensional analysis

(also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit

unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

temperature

intensive property representing the hotness or coldness of matter

unit conversion factor

ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

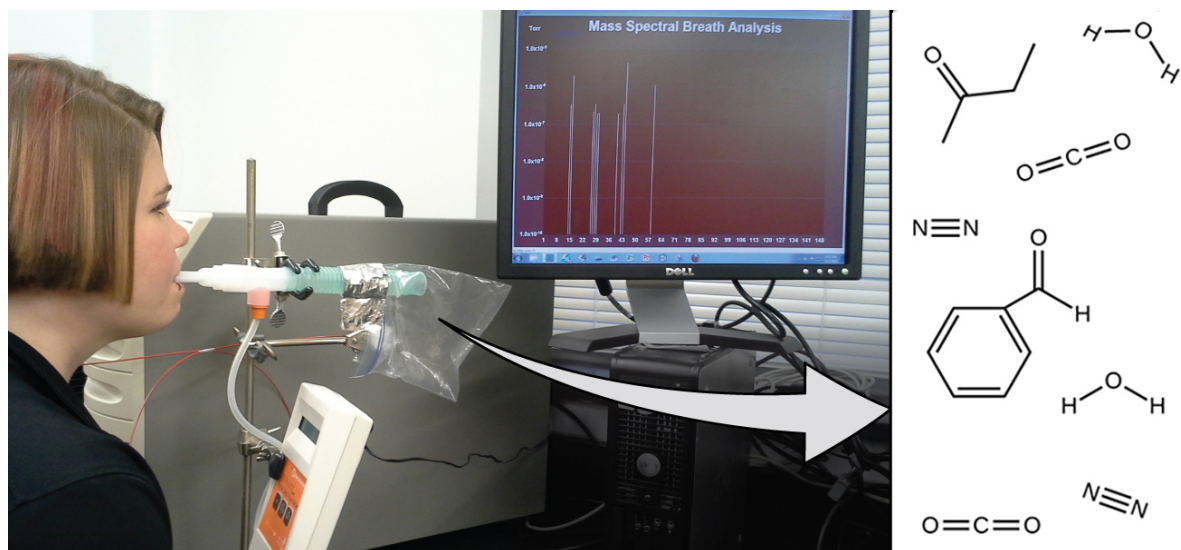
## Introduction

class="introduction"

- Early Ideas in Atomic Theory
- Evolution of Atomic Theory
- Atomic Structure and Symbolism
- Chemical Formulas

Analysis of  
molecules in  
an exhaled  
breath can  
provide  
valuable  
information,  
leading to  
early  
diagnosis of  
diseases or  
detection of  
environmenta  
l exposure to  
harmful  
substances.

(credit:  
modification  
of work by  
Paul Flowers)



Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, the variability of the composition of isotopes, ion formation, chemical bonds in ionic and covalent compounds, the types of chemical reactions, and the naming of compounds.

## Early Ideas in Atomic Theory

By the end of this section, you will be able to:

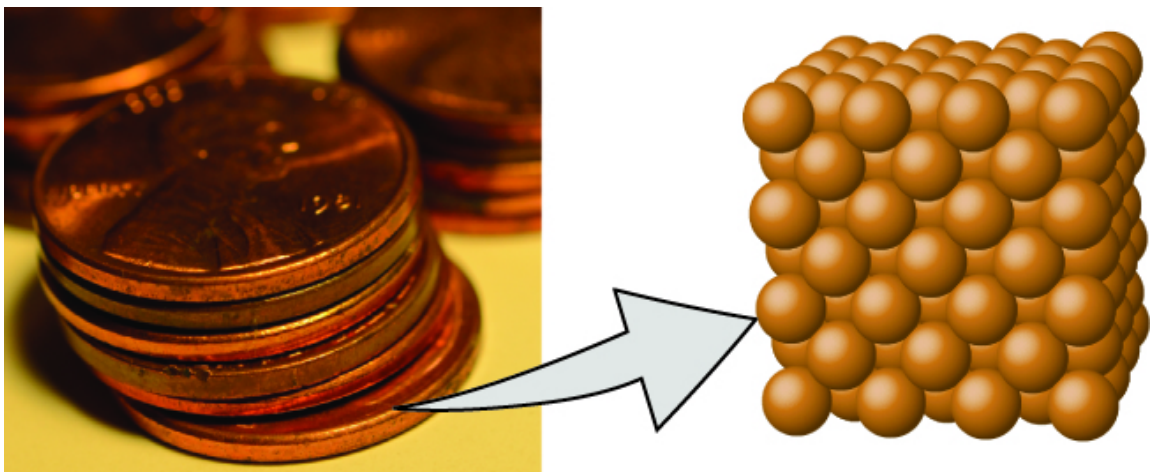
- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for “indivisible.” They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four “elements”—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and “elements” as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of **Dalton's atomic theory**.

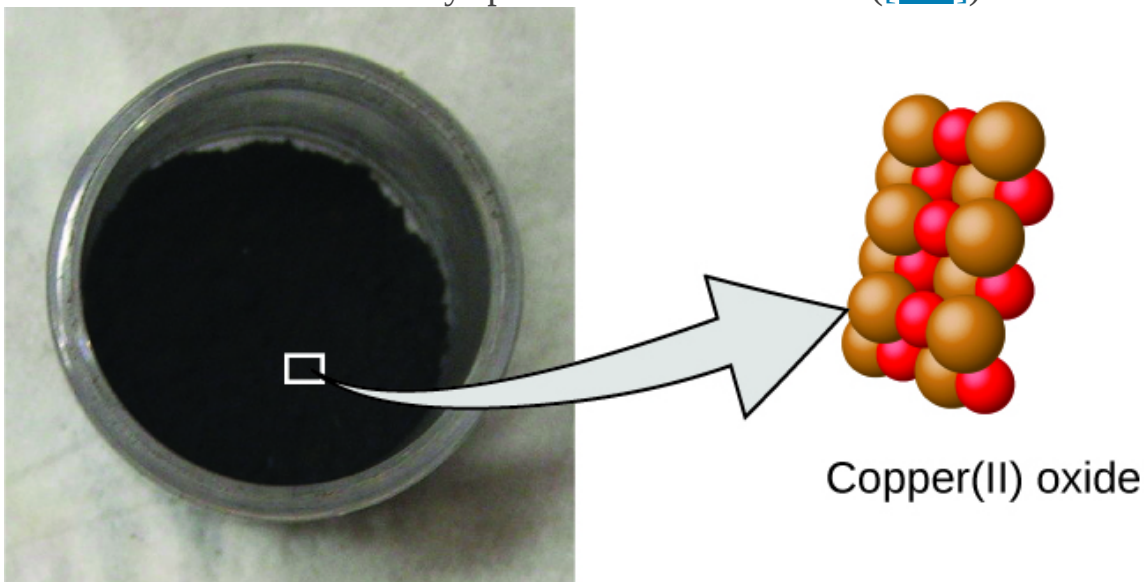
1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element ([\[link\]](#)). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.





A pre-1982 copper penny (left) contains approximately  $3 \times 10^{22}$  copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by “slgckgc”/Flickr)

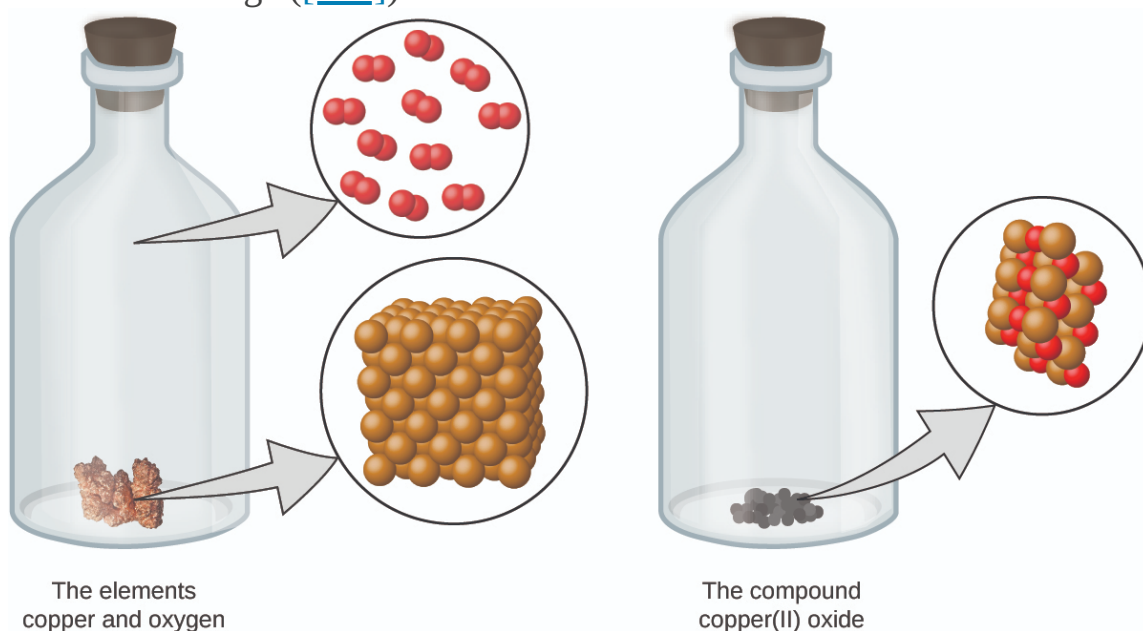
3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio ([\[link\]](#)).



Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and

oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by “Chemicalinterest”/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change ([link](#)).



When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by <http://images-of-elements.com/copper.php>)

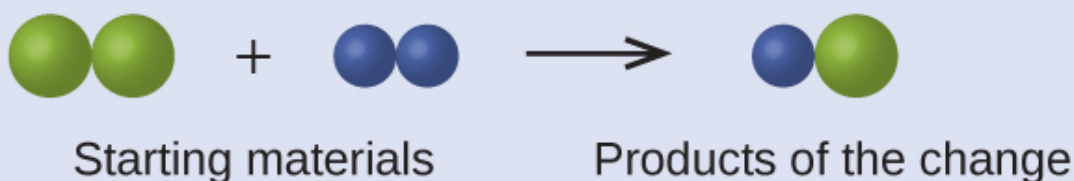
Dalton’s atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you’ve learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes

from one type to another will remain constant (the law of conservation of matter).

**Example:**

**Testing Dalton's Atomic Theory**

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

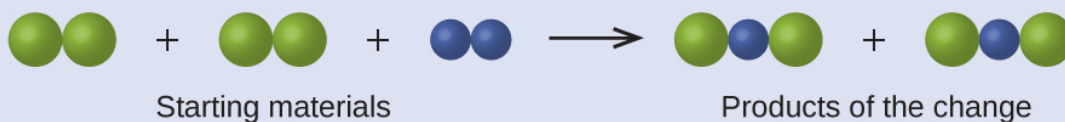


**Solution**

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

**Check Your Learning**

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



**Note:**

**Answer:**

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the **law of definite proportions** or the **law of constant composition**. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in [\[link\]](#).

Constant Composition of Isooctane			
Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82 \text{ g carbon}}{2.78 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33 \text{ g carbon}}{4.19 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40 \text{ g carbon}}{3.63 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there

are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

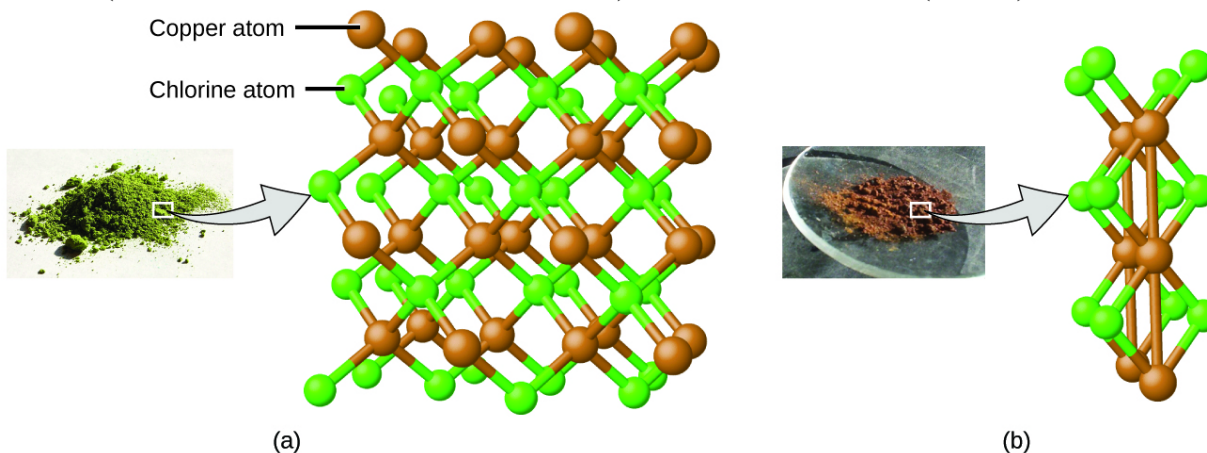
Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The **law of multiple proportions** states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

**Equation:**

$$\frac{\frac{1.116 \text{ g Cl}}{1 \text{ g Cu}}}{\frac{0.558 \text{ g Cl}}{1 \text{ g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 ([\[link\]](#)).



Compared to the copper chlorine compound in (a), where copper is

represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by “Benjah-bmm27”/Wikimedia Commons; credit b: modification of work by “Walkerma”/Wikimedia Commons)

**Example:****Laws of Definite and Multiple Proportions**

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

**Solution**

In compound A, the mass ratio of carbon to oxygen is:

**Equation:**

$$\frac{1.33 \text{ g O}}{1 \text{ g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

**Equation:**

$$\frac{2.67 \text{ g O}}{1 \text{ g C}}$$

The ratio of these ratios is:

**Equation:**

$$\frac{\frac{1.33 \text{ g O}}{1 \text{ g C}}}{\frac{2.67 \text{ g O}}{1 \text{ g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO<sub>2</sub>.

### Check Your Learning

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

### Note:

### Answer:

In compound X, the mass ratio of carbon to hydrogen is  $\frac{14.13 \text{ g C}}{2.96 \text{ g H}}$ . In compound Y, the mass ratio of carbon to hydrogen is  $\frac{19.91 \text{ g C}}{3.34 \text{ g H}}$ . The ratio of these ratios is  $\frac{\frac{14.13 \text{ g C}}{2.96 \text{ g H}}}{\frac{19.91 \text{ g C}}{3.34 \text{ g H}}} = \frac{4.77 \text{ g C/g H}}{5.96 \text{ g C/g H}} = 0.800 = \frac{4}{5}$ . This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

## Key Concepts and Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small,

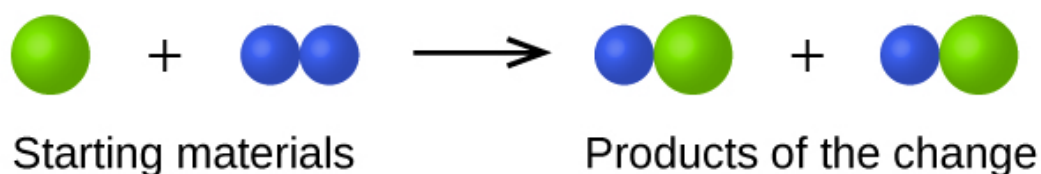
whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?



---

#### Solution:

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that atoms are not created during a chemical change, but are merely redistributed.

### Exercise:

#### Problem:

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

### Exercise:



**Problem:**

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

---

**Solution:**

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

**Exercise:****Problem:**

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you

about compounds X, Y, and Z?

## **Glossary**

Dalton's atomic theory

set of postulates that established the fundamental properties of atoms

law of constant composition

(also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of definite proportions

(also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions

when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

## Evolution of Atomic Theory

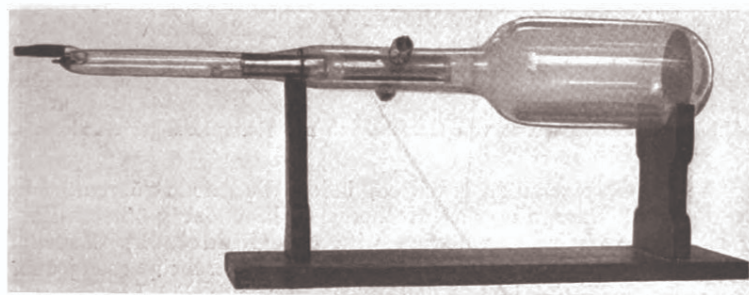
By the end of this section, you will be able to:

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Define isotopes and give examples for several elements

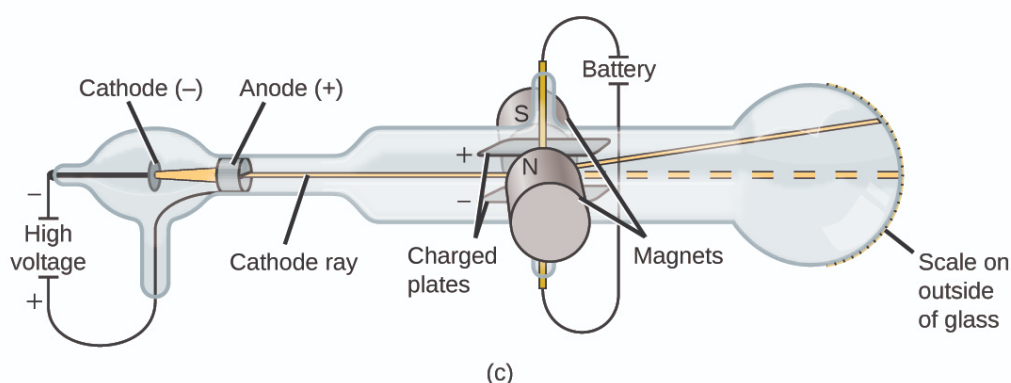
If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms ([link](#)).



(a)



(b)



(c)

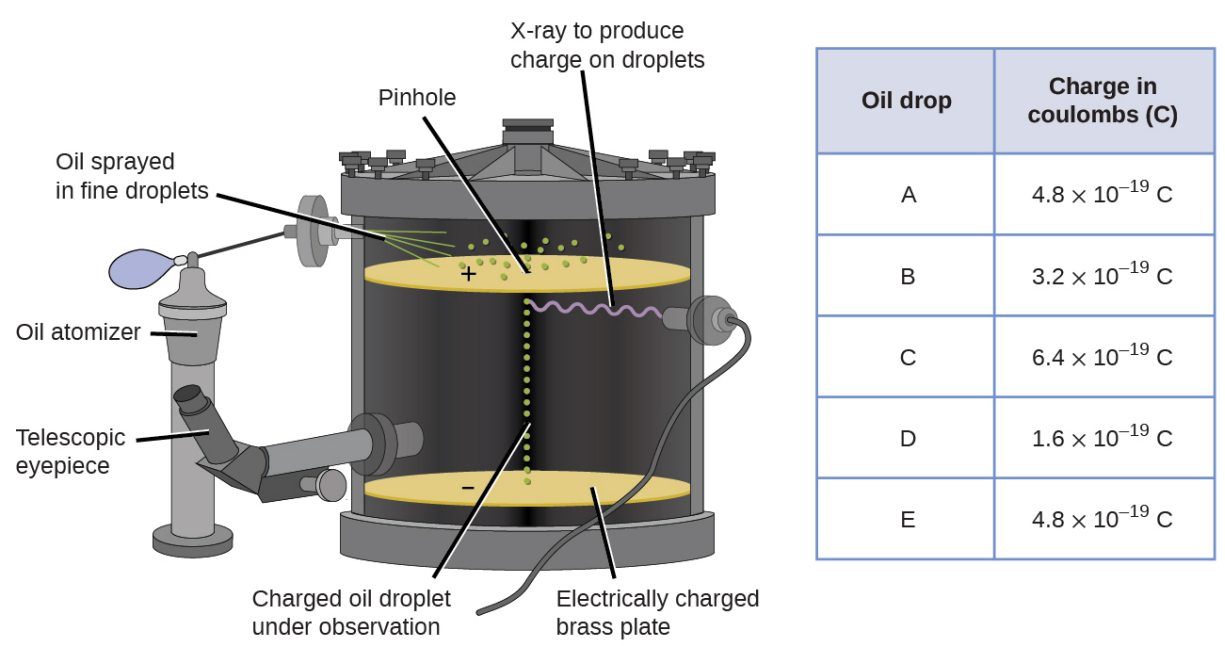
(a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by “Kurzon”/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (–) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson’s idea was gradually accepted, and his cathode ray particle is what we now call an **electron**, a negatively charged, subatomic

particle with a mass more than one thousand-times less that of an atom. The term “electron” was coined in 1891 by Irish physicist George Stoney, from “*electric ion.*”

**Note:**  
Click [here](#) to hear Thomson describe his discovery in his own voice.

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops ([link](#)).



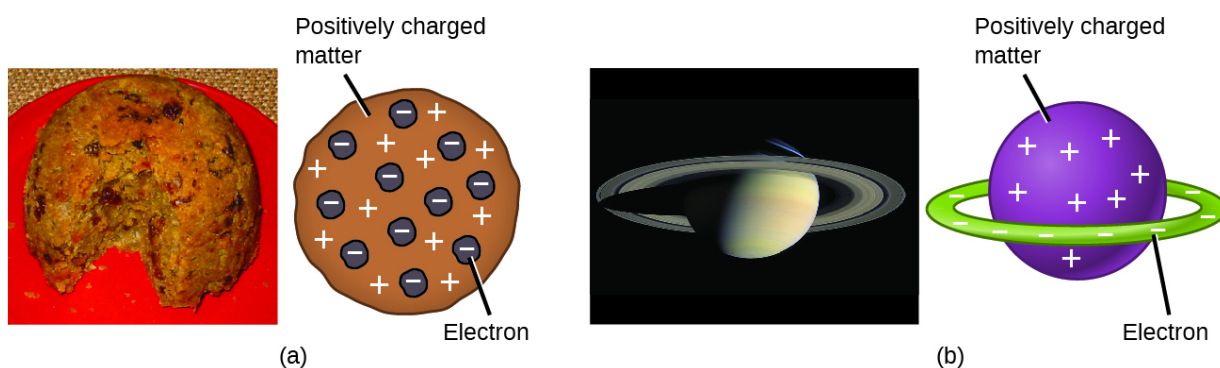
Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge,  $1.6 \times 10^{-19} \text{ C}$ . Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times  $1.6 \times 10^{-19} \text{ C}$ ), two electrons (2 times  $1.6 \times 10^{-19} \text{ C}$ ), three electrons (3 times  $1.6 \times 10^{-19} \text{ C}$ ), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan’s research, and the charge-to-mass ratio was already known due to Thomson’s research ( $1.759 \times 10^{11} \text{ C/kg}$ ), it only required a simple calculation to determine the mass of the electron as well.

**Equation:**

$$\text{Mass of electron} = 1.602 \times 10^{-19} \text{ C} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \text{ C}} = 9.107 \times 10^{-31} \text{ kg}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons ([\[link\]](#)).



- (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man

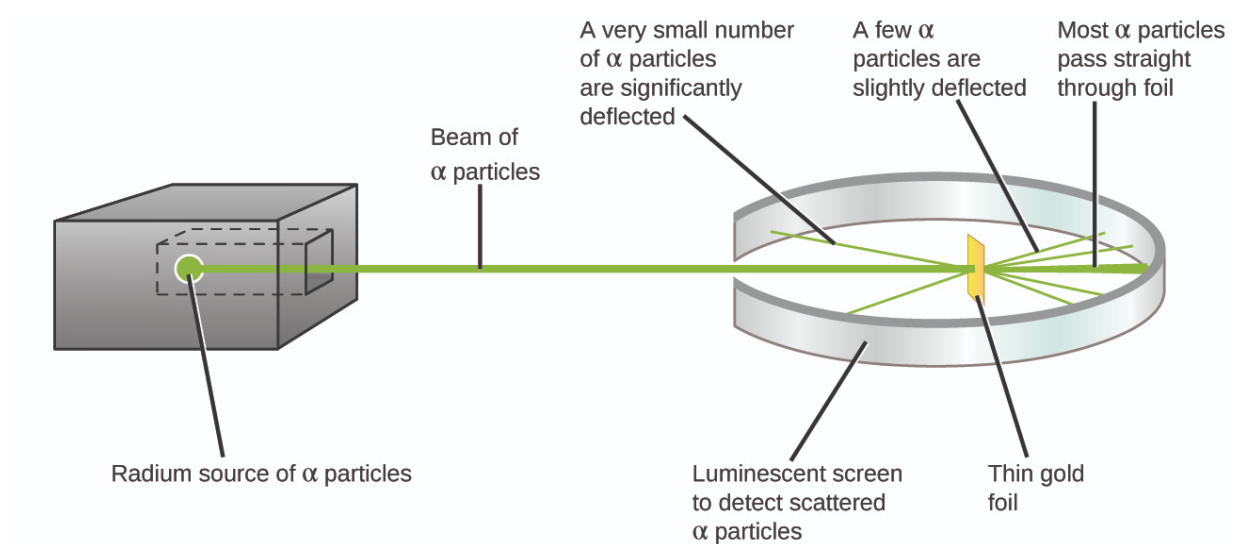
vyi”/Wikimedia Commons; credit b: modification of work by  
“NASA”/Wikimedia Commons)

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged **alpha particles ( $\alpha$  particles)** that were produced by the radioactive decay of radium;  $\alpha$  particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of  $\alpha$  particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the  $\alpha$  particles using a luminescent screen that glowed briefly where hit by an  $\alpha$  particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source ([\[link\]](#)). Rutherford described finding these results: “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.”[\[footnote\]](#)

Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014,

<https://ia600508.us.archive.org/3/items/backgroundtomode032734mbp/backgroundtomode032734mbp.pdf>.



Geiger and Rutherford fired  $\alpha$  particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving  $\alpha$  particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged  $\alpha$  particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the **nucleus**, must be at the center of each atom.

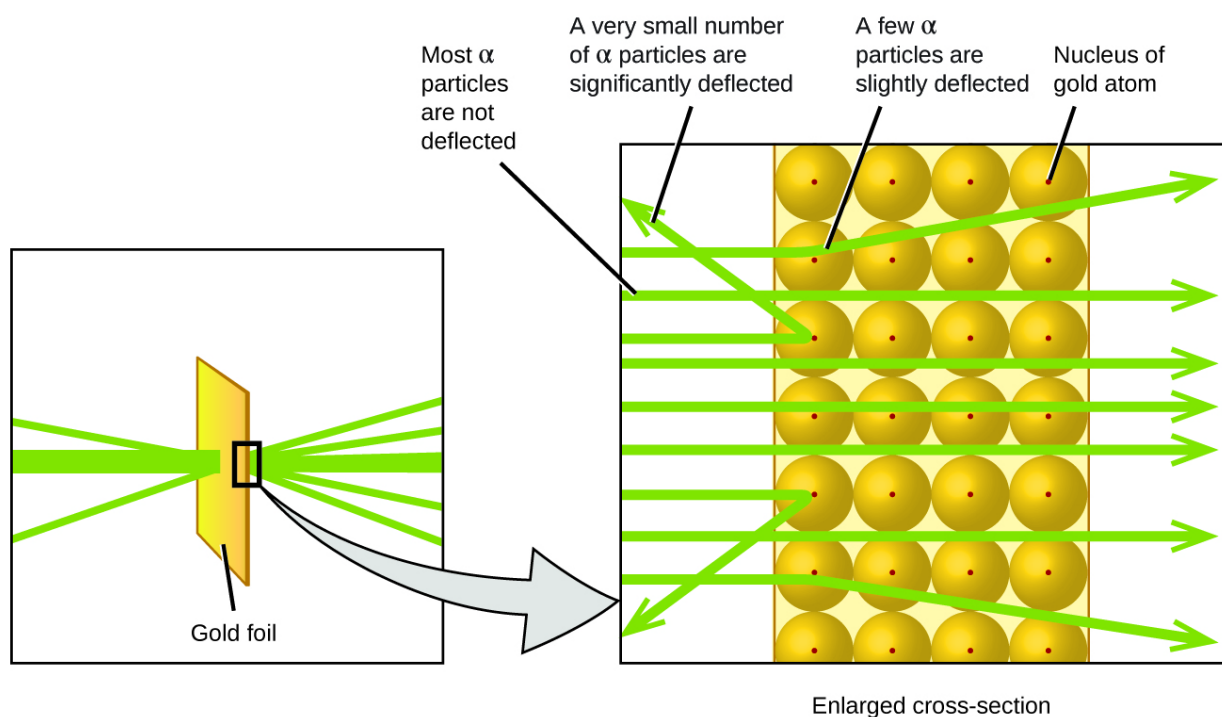
**Note:**

View this [simulation](#) of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of  $\alpha$  particles to see how that affects the



scattering pattern.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral ([link](#)). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a “building block,” and he named this more fundamental particle the **proton**, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.



The  $\alpha$  particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few  $\alpha$  particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

**Note:**

The [Rutherford Scattering simulation](#) allows you to investigate the differences between a “plum pudding” atom and a Rutherford atom by firing  $\alpha$  particles at each type of atom.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a “new element” produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called **isotopes**—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of **neutrons**, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later.

## Key Concepts and Summary

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson’s cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford’s gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

---

#### Solution:

Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

### Exercise:

**Problem:** How are electrons and protons similar? How are they different?

### Exercise:

**Problem:** How are protons and neutrons similar? How are they different?

---

#### Solution:

Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

### Exercise:

#### Problem:

Predict and test the behavior of  $\alpha$  particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by  $\alpha$  particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the  $\alpha$  particles to take these paths.

(b) If  $\alpha$  particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy  $\alpha$  particle

paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the [Rutherford Scattering simulation](#) and select the “Plum Pudding Atom” tab. Set “Alpha Particles Energy” to “min,” and select “show traces.” Click on the gun to start firing  $\alpha$  particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or “Reset All.” Set “Alpha Particles Energy” to “max,” and start firing  $\alpha$  particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

### **Exercise:**

#### **Problem:**

Predict and test the behavior of  $\alpha$  particles fired at a Rutherford atom model.

(a) Predict the paths taken by  $\alpha$  particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the  $\alpha$  particles to take these paths.

(b) If  $\alpha$  particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy  $\alpha$  particle paths. Explain your reasoning.

(c) Predict how the paths taken by the  $\alpha$  particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the [Rutherford Scattering simulation](#) and select the “Rutherford Atom” tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select “20” for both protons and neutrons, “min” for energy, show traces, and then start firing  $\alpha$  particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to “max,” and start firing  $\alpha$  particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select “40” for both protons and neutrons, “min” for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of  $\alpha$  particles? Be clear and specific.

---

**Solution:**

(a) The Rutherford atom has a small, positively charged nucleus, so most  $\alpha$  particles will pass through empty space far from the nucleus and be undeflected. Those  $\alpha$  particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the  $\alpha$  particles are headed, the larger the deflection angle will be. (b) Higher-energy  $\alpha$  particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the  $\alpha$  particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more  $\alpha$  particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the  $\alpha$  particles match the predictions from (a), (b), and (c).

**Glossary**

alpha particle ( $\alpha$  particle)

positively charged particle consisting of two protons and two neutrons

electron

negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes

atoms that contain the same number of protons but different numbers of neutrons

neutron

uncharged, subatomic particle located in the nucleus

nucleus

massive, positively charged center of an atom made up of protons and neutrons

proton

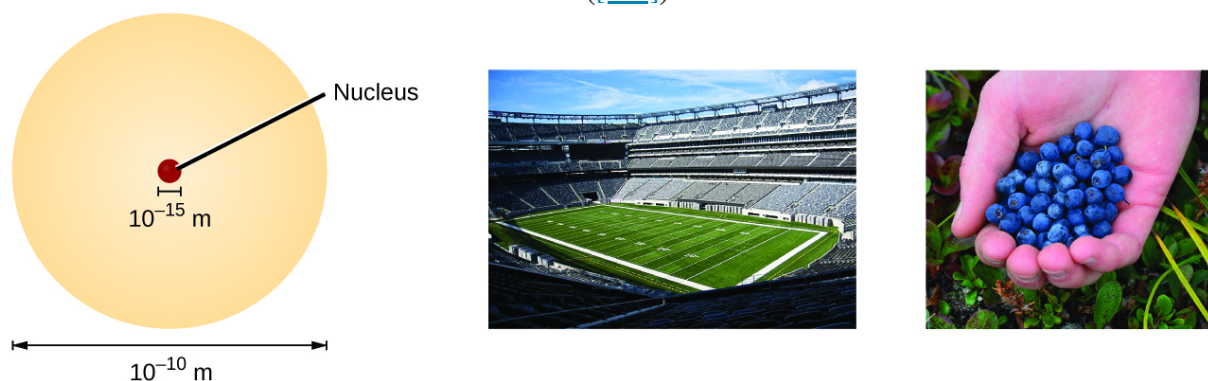
positively charged, subatomic particle located in the nucleus

## Atomic Structure and Symbolism

By the end of this section, you will be able to:

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of  $10^{-10}$  m, whereas the diameter of the nucleus is roughly  $10^{-15}$  m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium ([link](#)).



If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by “babyknight”/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than  $2 \times 10^{-23}$  g, and an electron has a charge of less than  $2 \times 10^{-19}$  C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the **atomic mass unit (amu)** and the **fundamental unit of charge (e)**. The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as “carbon-12” as will be discussed later in this module.) Thus, one amu is exactly  $\frac{1}{12}$  of the mass of one carbon-12 atom:  $1 \text{ amu} = 1.6605 \times 10^{-24}$  g. (The **Dalton (Da)** and the **unified atomic mass unit (u)** are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with  $e = 1.602 \times 10^{-19}$  C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1– and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton). The properties of these fundamental particles are summarized in [link](#). (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00

amu. This “missing” mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Properties of Subatomic Particles					
Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	$-1.602 \times 10^{-19}$	1−	0.00055	$0.00091 \times 10^{-24}$
proton	nucleus	$1.602 \times 10^{-19}$	1+	1.00727	$1.67262 \times 10^{-24}$
neutron	nucleus	0	0	1.00866	$1.67493 \times 10^{-24}$

The number of protons in the nucleus of an atom is its **atomic number (Z)**. This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its **mass number (A)**. The number of neutrons is therefore the difference between the mass number and the atomic number:  $A - Z$  = number of neutrons.

**Equation:**

$$\begin{aligned}\text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ A - Z &= \text{number of neutrons}\end{aligned}$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**. Positively charged atoms called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom ( $Z = 11$ ) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge ( $11 - 10 = 1+$ ). A neutral oxygen atom ( $Z = 8$ ) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge ( $8 - 10 = 2-$ ).

**Example:****Composition of an Atom**

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland ([link](#)).



(a)



(b)

(a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a  $1^-$  charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

**Solution**

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 ( $127 - 53 = 74$ ). Since the iodine is added as a  $1^-$  anion, the number of electrons is 54 [ $53 - (1^-) = 54$ ].

**Check Your Learning**

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

**Note:****Answer:**

78 protons; 117 neutrons; charge is  $4+$

**Chemical Symbols**



A **chemical symbol** is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg ([link](#)). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The symbols for several common elements and their atoms are listed in [link](#). Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table in [link](#) (also found in [link](#)).

Some Common Elements and Their Symbols			
Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from <i>ferrum</i> )

Some Common Elements and Their Symbols			
Element	Symbol	Element	Symbol
bromine	Br	lead	Pb (from <i>plumbum</i> )
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from <i>hydrargyrum</i> )
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from <i>kalium</i> )
copper	Cu (from <i>cuprum</i> )	silicon	Si
fluorine	F	silver	Ag (from <i>argentum</i> )
gold	Au (from <i>aurum</i> )	sodium	Na (from <i>natrium</i> )
helium	He	sulfur	S
hydrogen	H	tin	Sn (from <i>stannum</i> )
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists (or occasionally locations); for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

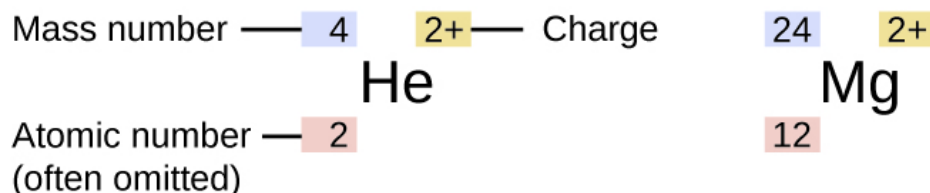
**Note:**

Visit this [site](#) to learn more about IUPAC, the International Union of Pure and Applied Chemistry, and explore its periodic table.

## Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol ([link](#)). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ , and  $^{26}\text{Mg}$ . These isotope symbols are read as “element, mass number” and can be symbolized consistent with this reading.

For instance,  $^{24}\text{Mg}$  is read as “magnesium 24,” and can be written as “magnesium-24” or “Mg-24.”  $^{25}\text{Mg}$  is read as “magnesium 25,” and can be written as “magnesium-25” or “Mg-25.” All magnesium atoms have 12 protons in their nucleus. They differ only because a  $^{24}\text{Mg}$  atom has 12 neutrons in its nucleus, a  $^{25}\text{Mg}$  atom has 13 neutrons, and a  $^{26}\text{Mg}$  has 14 neutrons.



The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in [\[link\]](#). Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized  $^2\text{H}$ , is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized  $^3\text{H}$ , is also called tritium and sometimes symbolized T.

Nuclear Compositions of Atoms of the Very Light Elements						
Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^1_1\text{H}$ (protium)	1	1	0	1.0078	99.989
	$^2_1\text{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^3_1\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^3_2\text{He}$	2	2	1	3.01603	0.00013
	$^4_2\text{He}$	2	2	2	4.0026	100
lithium	$^6_3\text{Li}$	3	3	3	6.0151	7.59

Nuclear Compositions of Atoms of the Very Light Elements						
Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
	${}^7_3\text{Li}$	3	3	4	7.0160	92.41
beryllium	${}^9_4\text{Be}$	4	4	5	9.0122	100
boron	${}^{10}_5\text{B}$	5	5	5	10.0129	19.9
	${}^{11}_5\text{B}$	5	5	6	11.0093	80.1
carbon	${}^{12}_6\text{C}$	6	6	6	12.0000	98.89
	${}^{13}_6\text{C}$	6	6	7	13.0034	1.11
	${}^{14}_6\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	${}^{14}_7\text{N}$	7	7	7	14.0031	99.63
	${}^{15}_7\text{N}$	7	7	8	15.0001	0.37
oxygen	${}^{16}_8\text{O}$	8	8	8	15.9949	99.757
	${}^{17}_8\text{O}$	8	8	9	16.9991	0.038
	${}^{18}_8\text{O}$	8	8	10	17.9992	0.205
fluorine	${}^{19}_9\text{F}$	9	9	10	18.9984	100
neon	${}^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
	${}^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	${}^{22}_{10}\text{Ne}$	10	10	12	21.9914	9.25

**Note:**

Use this [Build an Atom simulator](#) to build atoms of the first 10 elements, see which isotopes exist, check nuclear stability, and gain experience with isotope symbols.

## Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the **atomic mass** of a single atom is approximately equal to its mass number (a

whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

**Equation:**

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are  $^{10}\text{B}$  with a mass of 10.0129 amu, and the remaining 80.1% are  $^{11}\text{B}$  with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

**Equation:**

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129 \text{ amu}) + (0.801 \times 11.0093 \text{ amu}) \\ &= 1.99 \text{ amu} + 8.82 \text{ amu} \\ &= 10.81 \text{ amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

**Example:**

#### Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84%  $^{20}\text{Ne}$  (mass 19.9924 amu), 0.47%  $^{21}\text{Ne}$  (mass 20.9940 amu), and 7.69%  $^{22}\text{Ne}$  (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

**Solution**

**Equation:**

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924 \text{ amu}) + (0.0047 \times 20.9940 \text{ amu}) + (0.0769 \times 21.9914 \text{ amu}) \\ &= (18.36 + 0.099 + 1.69) \text{ amu} \\ &= 20.15 \text{ amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

#### Check Your Learning

A sample of magnesium is found to contain 78.70% of  $^{24}\text{Mg}$  atoms (mass 23.98 amu), 10.13% of  $^{25}\text{Mg}$  atoms (mass 24.99 amu), and 11.17% of  $^{26}\text{Mg}$  atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

**Note:**

**Answer:**

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

**Example:**

**Calculation of Percent Abundance**

Naturally occurring chlorine consists of  $^{35}\text{Cl}$  (mass 34.96885 amu) and  $^{37}\text{Cl}$  (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

**Solution**

The average mass of chlorine is the fraction that is  $^{35}\text{Cl}$  times the mass of  $^{35}\text{Cl}$  plus the fraction that is  $^{37}\text{Cl}$  times the mass of  $^{37}\text{Cl}$ .

**Equation:**

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let  $x$  represent the fraction that is  $^{35}\text{Cl}$ , then the fraction that is  $^{37}\text{Cl}$  is represented by  $1.00 - x$ . (The fraction that is  $^{35}\text{Cl}$  + the fraction that is  $^{37}\text{Cl}$  must add up to 1, so the fraction of  $^{37}\text{Cl}$  must equal  $1.00 - \text{the fraction of } ^{35}\text{Cl}$ .)

Substituting this into the average mass equation, we have:

**Equation:**

$$\begin{aligned} 35.453 \text{ amu} &= (x \times 34.96885 \text{ amu}) + [(1.00 - x) \times 36.96590 \text{ amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576 \end{aligned}$$

So solving yields:  $x = 0.7576$ , which means that  $1.00 - 0.7576 = 0.2424$ . Therefore, chlorine consists of 75.76%  $^{35}\text{Cl}$  and 24.24%  $^{37}\text{Cl}$ .

**Check Your Learning**

Naturally occurring copper consists of  $^{63}\text{Cu}$  (mass 62.9296 amu) and  $^{65}\text{Cu}$  (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

**Note:**

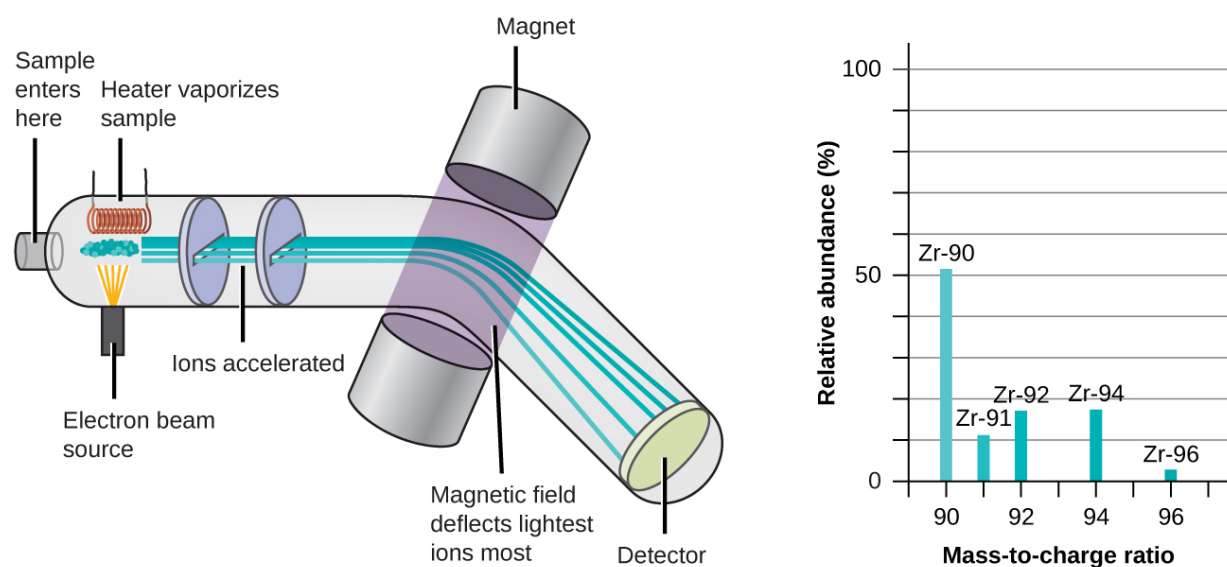
**Answer:**

69.15% Cu-63 and 30.85% Cu-65

**Note:**

Visit this [site](#) to make mixtures of the main isotopes of the first 18 elements, gain experience with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer ([link](#)), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent than that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

**Note:**

See an [animation](#) that explains mass spectrometry. Watch this [video](#) from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

## Key Concepts and Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one

atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly  $\frac{1}{12}$  of the mass of a carbon-12 atom and is equal to  $1.6605 \times 10^{-24}$  g.

Protons are relatively heavy particles with a charge of  $1+$  and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of  $1-$  and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

## Key Equations

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

In what way are isotopes of a given element always different? In what way(s) are they always the same?

### Exercise:

**Problem:** Write the symbol for each of the following ions:

- (a) the ion with a  $1+$  charge, atomic number 55, and mass number 133
- (b) the ion with 54 electrons, 53 protons, and 74 neutrons
- (c) the ion with atomic number 15, mass number 31, and a  $3-$  charge
- (d) the ion with 24 electrons, 30 neutrons, and a  $3+$  charge

---

#### Solution:

(a)  $^{133}\text{Cs}^+$ ; (b)  $^{127}\text{I}^-$ ; (c)  $^{31}\text{P}^{3-}$ ; (d)  $^{57}\text{Co}^{3+}$

### Exercise:



**Problem:** Write the symbol for each of the following ions:

- (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71
- (b) the ion with 36 electrons, 35 protons, and 45 neutrons
- (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge
- (d) the ion with a 2+ charge, atomic number 38, and mass number 87

**Exercise:**

**Problem:** Open the [Build an Atom simulation](#) and click on the Atom icon.

- (a) Pick any one of the first 10 elements that you would like to build and state its symbol.
- (b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.
- (c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.
- (d) Predict whether your atom will be stable or unstable. State your reasoning.
- (e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

---

**Solution:**

(a) Carbon-12,  $^{12}\text{C}$ ; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral  $^{12}\text{C}$  atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

**Exercise:**

**Problem:** Open the [Build an Atom simulation](#)

- (a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.
- (b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

**Exercise:**

**Problem:** Open the [Build an Atom simulation](#)

- (a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.
- (b) Now remove one electron to make an ion and give the symbol for the ion you have created.

---

**Solution:**

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is  ${}^6\text{Li}$  or  ${}^6_3\text{Li}$ . (b)  ${}^6\text{Li}^+$  or  ${}^6_3\text{Li}^+$

**Exercise:**

**Problem:**

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

- (a) atomic number 9, mass number 18, charge of  $1^-$
- (b) atomic number 43, mass number 99, charge of  $7^+$
- (c) atomic number 53, atomic mass number 131, charge of  $1^-$
- (d) atomic number 81, atomic mass number 201, charge of  $1^+$
- (e) Name the elements in parts (a), (b), (c), and (d).

**Exercise:**

**Problem:**

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

- (a) atomic number 26, mass number 58, charge of  $2^+$
- (b) atomic number 53, mass number 127, charge of  $1^-$

---

**Solution:**

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

**Exercise:**

**Problem:**

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

- (a)  ${}^{10}_5\text{B}$
- (b)  ${}^{199}_{80}\text{Hg}$
- (c)  ${}^{63}_{29}\text{Cu}$
- (d)  ${}^{13}_6\text{C}$
- (e)  ${}^{77}_{34}\text{Se}$

**Exercise:**

**Problem:**

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

- (a)  ${}^7_3\text{Li}$
  - (b)  ${}^{125}_{52}\text{Te}$
  - (c)  ${}^{109}_{47}\text{Ag}$
  - (d)  ${}^{15}_7\text{N}$
  - (e)  ${}^{31}_{15}\text{P}$
- 

**Solution:**

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

**Exercise:**

**Problem:**

Click on the [site](#) and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

- (a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.
- (b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.
- (c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.
- (d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.
- (e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

**Exercise:**

**Problem:** Repeat [\[link\]](#) using an element that has three naturally occurring isotopes.

---

**Solution:**

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature’s mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

**Exercise:**

**Problem:**

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

**Exercise:****Problem:**

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes,  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

---

**Solution:**

79.90 amu

**Exercise:****Problem:**

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5%  $^6\text{Li}$  and 92.5%  $^7\text{Li}$ , which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75%  $^6\text{Li}$  (and the rest  $^7\text{Li}$ ). Calculate the average atomic mass values for each of these two sources.

**Exercise:****Problem:**

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses ( $^{10}\text{B}$ , 10.0129 amu and  $^{11}\text{B}$ , 11.00931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

---

**Solution:**

Turkey source: 20.3% (of 10.0129 amu isotope); US source: 19.1% (of 10.0129 amu isotope)

**Exercise:****Problem:**

The  $^{18}\text{O}$ : $^{16}\text{O}$  abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

**Glossary**

anion

negatively charged atom or molecule (contains more electrons than protons)

atomic mass

average mass of atoms of an element, expressed in amu

atomic mass unit (amu)

(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to  $\frac{1}{12}$  of the mass of a  $^{12}\text{C}$  atom

atomic number (Z)

number of protons in the nucleus of an atom

cation

positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol

one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)

alternative unit equivalent to the atomic mass unit

fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron (e) with  $e = 1.602 \times 10^{-19} \text{ C}$

ion

electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

## Chemical Formulas

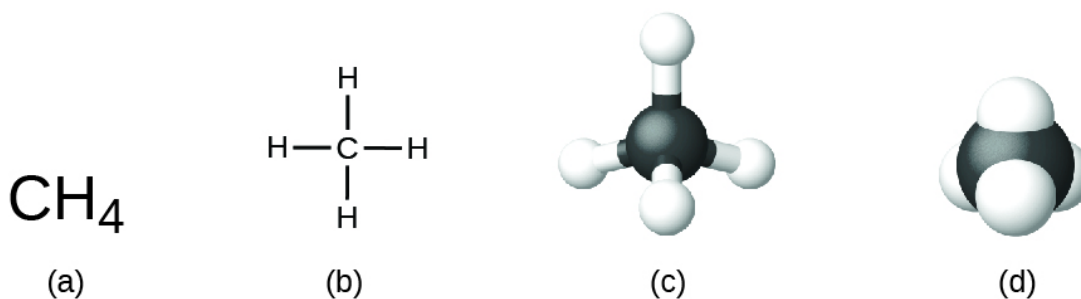
By the end of this section, you will be able to:

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas
- Define the amount unit mole and the related quantity Avogadro's number
- Explain the relation between mass, moles, and numbers of atoms or molecules and perform calculations deriving these quantities from one another

## Molecular and Empirical Formulas

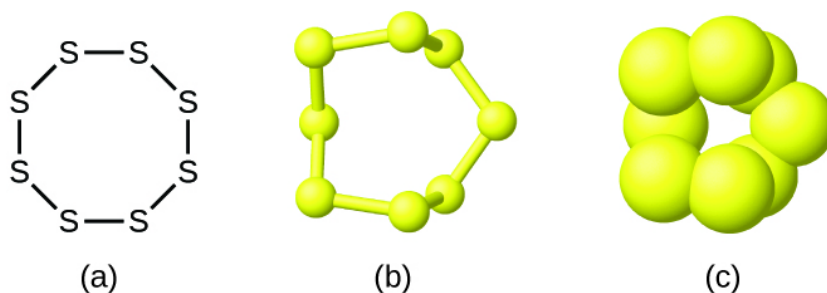
A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule ([\[link\]](#)). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.



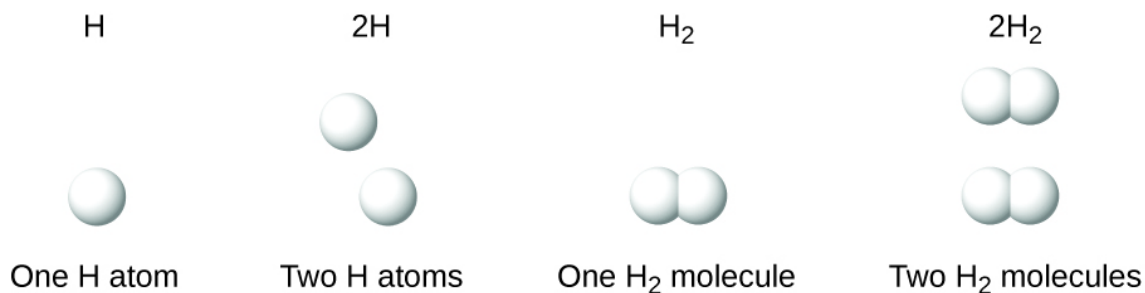
A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$ , respectively. Other elements commonly found as diatomic molecules are fluorine ( $\text{F}_2$ ), chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ), and iodine ( $\text{I}_2$ ). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is  $\text{S}_8$  ([link](#)).



A molecule of sulfur is composed of eight sulfur atoms and is therefore written as  $\text{S}_8$ . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example,  $\text{H}_2$  and  $2\text{H}$  represent distinctly different species.  $\text{H}_2$  is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression  $2\text{H}$ , on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression  $2\text{H}_2$  represents two molecules of diatomic hydrogen ([link](#)).

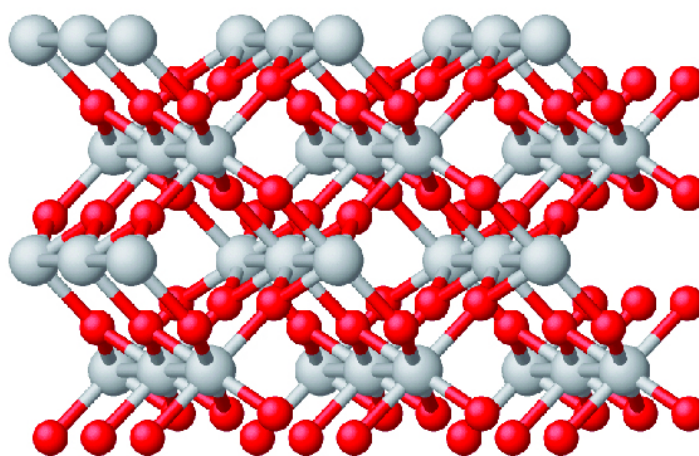


The symbols  $\text{H}$ ,  $2\text{H}$ ,  $\text{H}_2$ , and  $2\text{H}_2$  represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an **empirical formula**, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of  $\text{TiO}_2$ . This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium ([link](#)).



(a)

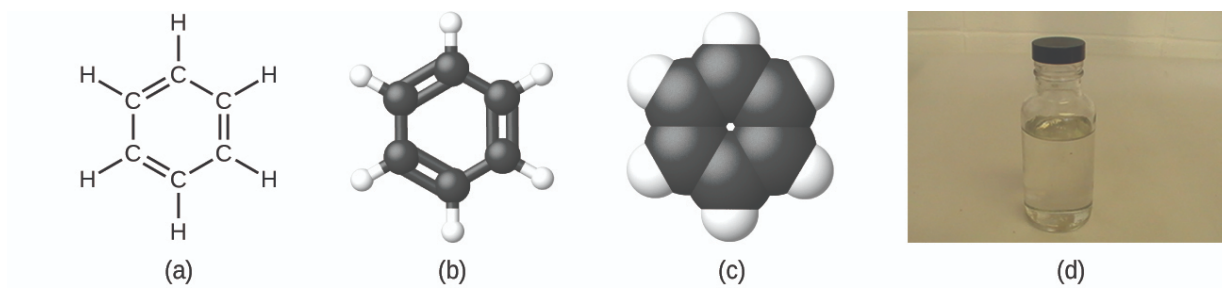


(b)

- (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide,  $\text{TiO}_2$ , contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr)

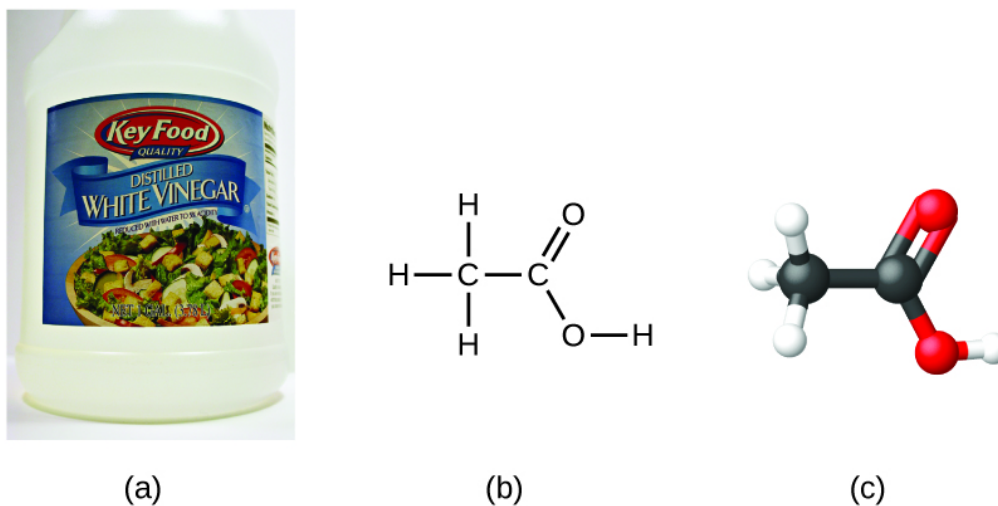
As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is  $\text{C}_6\text{H}_6$  ([link](#)).





Benzene,  $C_6H_6$ , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is  $C_2H_4O_2$ . This formula indicates that a molecule of acetic acid ([link](#)) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is  $CH_2O$ . Note that a molecular formula is always a whole-number multiple of an empirical formula.



(a) Vinegar contains acetic acid,  $C_2H_4O_2$ , which has an empirical formula of  $CH_2O$ . It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

**Example:****Empirical and Molecular Formulas**

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

**Solution**

The molecular formula is  $\text{C}_6\text{H}_{12}\text{O}_6$  because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is  $\text{CH}_2\text{O}$ .

**Check Your Learning**

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

**Note:****Answer:**

Molecular formula,  $\text{C}_8\text{H}_{16}\text{O}_4$ ; empirical formula,  $\text{C}_2\text{H}_4\text{O}$

**Note:**

You can explore [molecule building](#) using an online simulation.

**Note:****Lee Cronin**

What is it that chemists do? According to Lee Cronin ([link](#)), chemists make very complicated molecules by “chopping up” small molecules and “reverse engineering” them. He wonders if we could “make a really cool universal chemistry set” by what he calls “app-ing” chemistry. Could we “app” chemistry?

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical “inks” with a 3D printer capable of fabricating a reaction apparatus (tiny test tubes, beakers, and the like) to fashion a “universal toolkit of chemistry.” This toolkit could be used to create custom-tailored drugs to fight a new superbug or to “print” medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, “What Apple did for music, I’d like to do for the discovery and distribution of prescription drugs.”[\[footnote\]](#) View his [full talk](#) at the TED website.

Lee Cronin, “Print Your Own Medicine,” Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.

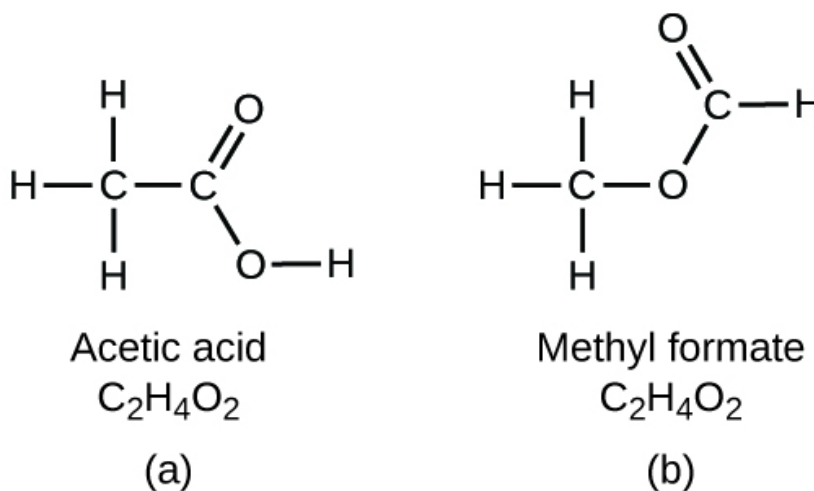


Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. The youngest chair at the University of Glasgow, Lee runs a large research group, collaborates with many scientists worldwide, has published over 250 papers in top scientific journals, and has given more than 150 invited talks. His research focuses on complex chemical systems and their potential to transform technology, but also branches into nanoscience, solar fuels, synthetic biology, and even artificial life and evolution. (credit: image courtesy of Lee Cronin)

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another

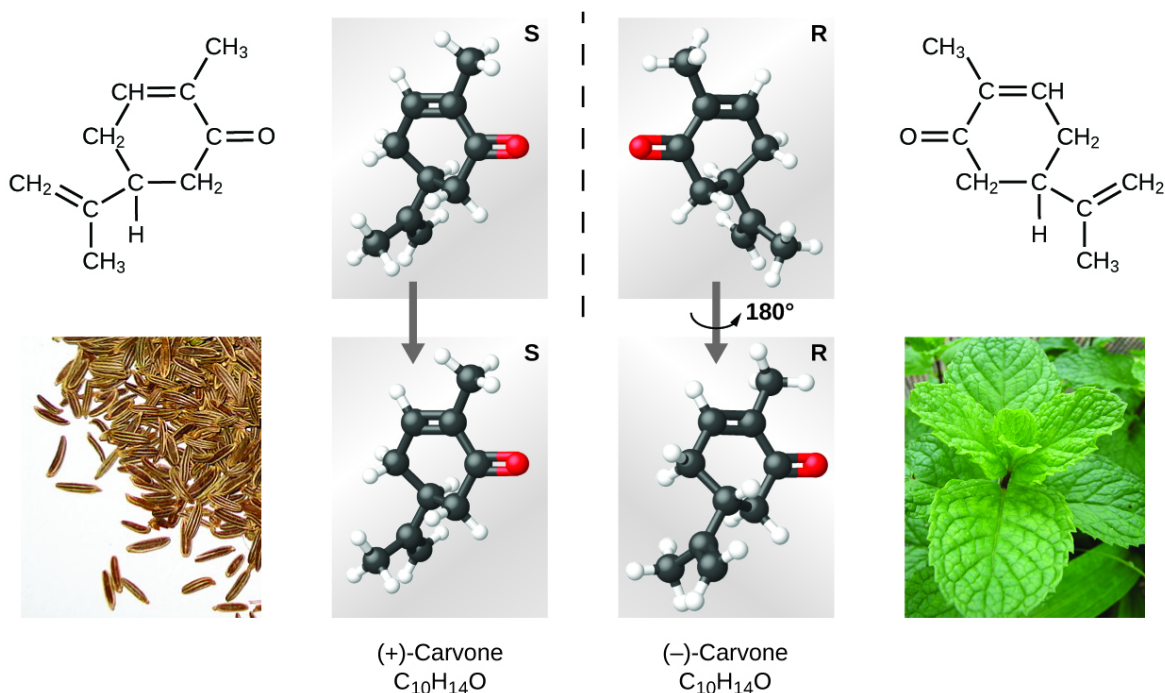
compound with the same formula as acetic acid,  $C_2H_4O_2$ ? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula  $C_2H_4O_2$  could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form a methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of **isomers**—compounds with the same chemical formula but different molecular structures ([link](#)). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.



Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ( $C_2H_4O_2$ ) but different structures (and therefore different chemical properties).

Many types of isomers exist ([link](#)). Acetic acid and methyl formate are **structural isomers**, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of **spatial isomers**, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(-)-carvone smells like spearmint.



Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by “Miansari66”/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

**Note:**

Select this [link](#) to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled “Mirror Molecule: Carvone”).

## The Mole

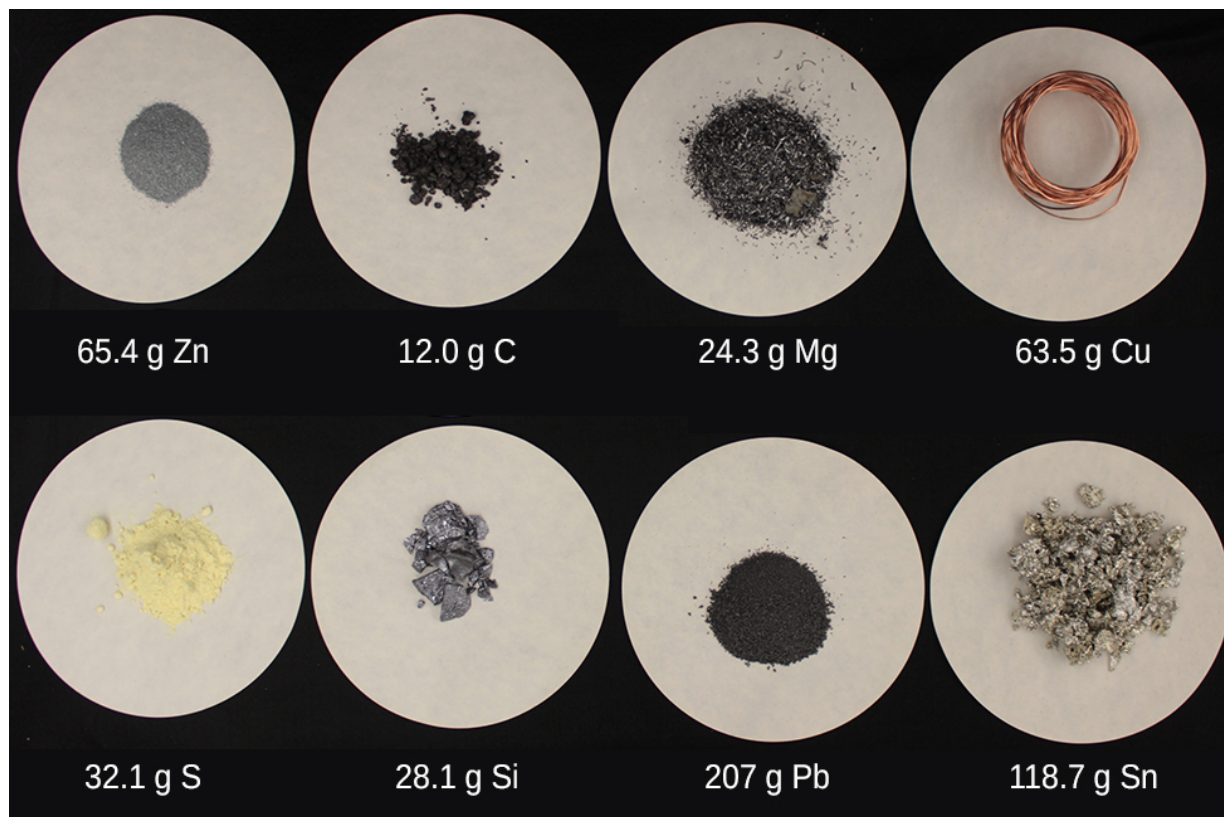
The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water,  $H_2O$ , and hydrogen peroxide,  $H_2O_2$ , are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental



approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The *mole* is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of the *number* of atoms or molecules in a sample of matter. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth. A **mole** of substance is that amount in which there are  $6.02214076 \times 10^{23}$  discrete entities (atoms or molecules). This large number is a fundamental constant known as **Avogadro's number ( $N_A$ )** or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of “per mole,” a conveniently rounded version being  $6.022 \times 10^{23}/\text{mol}$ .

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The **molar mass** of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see [\[link\]](#)).



Each sample contains  $6.022 \times 10^{23}$  atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to

right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

The molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single  $^{12}\text{C}$  atom weighs 12 amu (its atomic mass is 12 amu). A mole of  $^{12}\text{C}$  atoms weighs 12 g (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance,  $^{12}\text{C}$ . Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu ([link](#)).

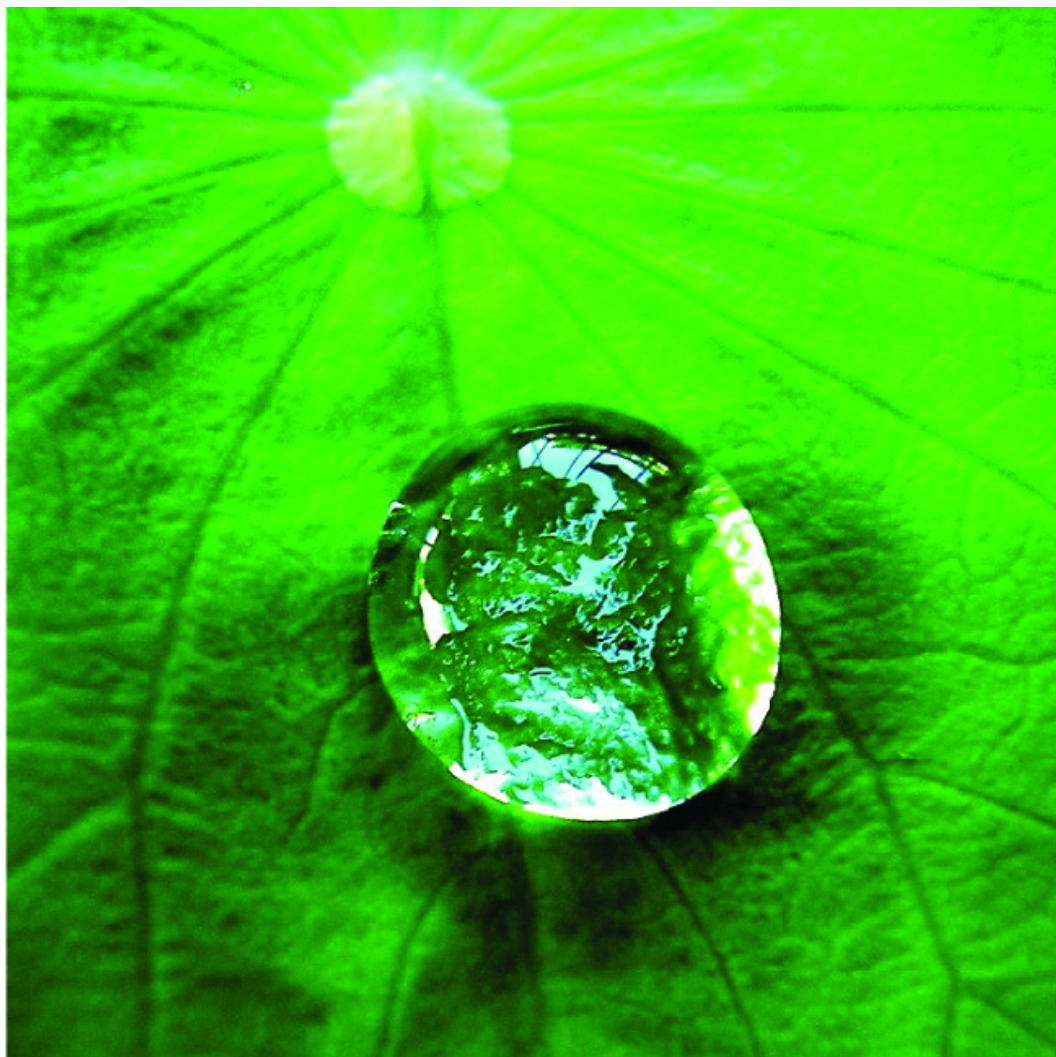


Each sample contains  $6.02 \times 10^{23}$  molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of  $\text{C}_8\text{H}_{17}\text{OH}$  (1-octanol, formula mass 130.2 amu), 454.4 g of  $\text{HgI}_2$  (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of  $\text{CH}_3\text{OH}$  (methanol, formula mass 32.0 amu) and 256.5 g of  $\text{S}_8$  (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	$6.022 \times 10^{23}$
H	1.008	1.008	$6.022 \times 10^{23}$
O	16.00	16.00	$6.022 \times 10^{23}$
Na	22.99	22.99	$6.022 \times 10^{23}$
Cl	35.45	35.45	$6.022 \times 10^{23}$

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see [\[link\]](#)). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.





The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: “tanakawho”/Wikimedia commons)

**Note:**

The mole is used in chemistry to represent  $6.022 \times 10^{23}$  of something, but it can be difficult to conceptualize such a large number. Watch this [video](#) and then complete the “Think” questions that follow. Explore more about the mole by reviewing the information under “Dig Deeper.”

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

**Example:**

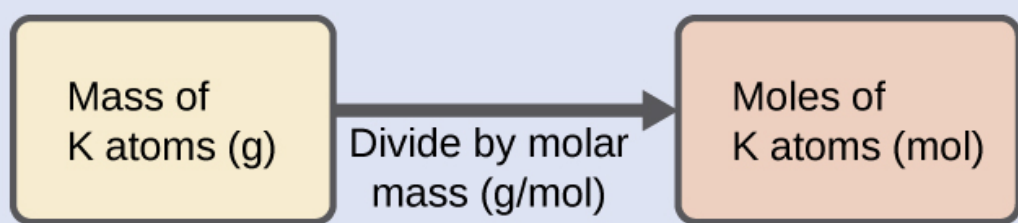
**Deriving Moles from Grams for an Element**

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

**Solution**

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

**Equation:**

$$4.7 \text{ g K} \left( \frac{\text{mol K}}{39.10 \text{ g}} \right) = 0.12 \text{ mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

**Check Your Learning**

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

**Note:**

**Answer:**

0.360 mol

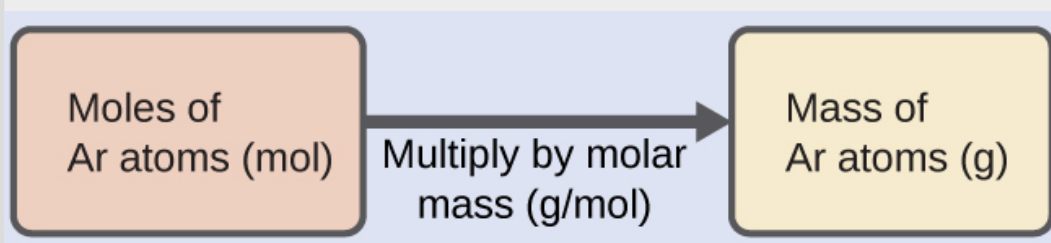
**Example:**

**Deriving Grams from Moles for an Element**

A liter of air contains  $9.2 \times 10^{-4}$  mol argon. What is the mass of Ar in a liter of air?

**Solution**

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth ( $\sim 10^{-3}$ ) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass ( $\sim 0.04$  g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

**Equation:**

$$9.2 \times 10^{-4} \text{ mol Ar} \left( \frac{39.95 \text{ g}}{\text{mol Ar}} \right) = 0.037 \text{ g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

**Check Your Learning**

What is the mass of 2.561 mol of gold?

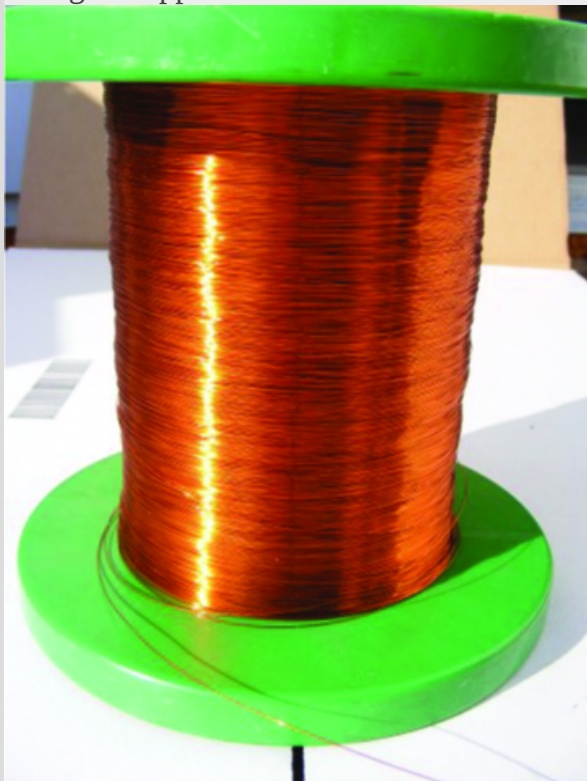
**Note:**

**Answer:**

504.4 g

**Example:****Deriving Number of Atoms from Mass for an Element**

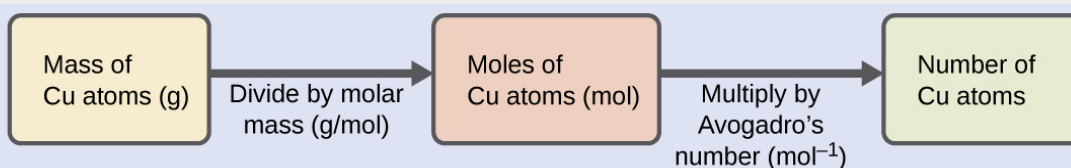
Copper is commonly used to fabricate electrical wire ([link](#)). How many copper atoms are in 5.00 g of copper wire?



Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

**Solution**

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number ( $N_A$ ) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth  $N_A$ , or approximately  $10^{22}$  Cu atoms. Carrying out the two-step computation yields:

**Equation:**

$$5.00 \text{ g Cu} \left( \frac{\cancel{\text{mol Cu}}}{63.55 \text{ g}} \right) \left( \frac{6.022 \times 10^{23} \text{ atoms}}{\cancel{\text{mol}}} \right) = 4.74 \times 10^{22} \text{ atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of  $10^{22}$  as expected.

**Check Your Learning**

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

**Note:****Answer:**

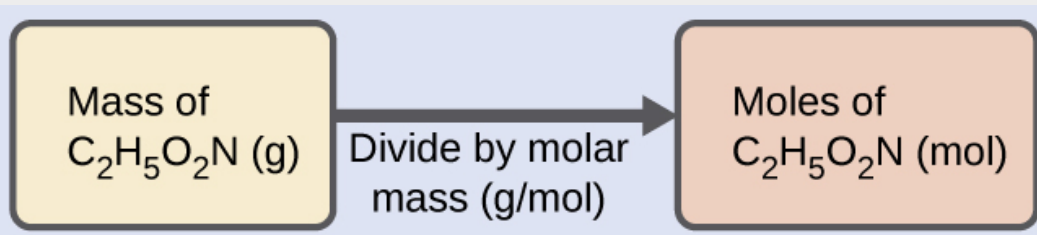
$4.586 \times 10^{22}$  Au atoms

**Example:****Deriving Moles from Grams for a Compound**

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula  $\text{C}_2\text{H}_5\text{O}_2\text{N}$ . How many moles of glycine molecules are contained in 28.35 g of glycine?

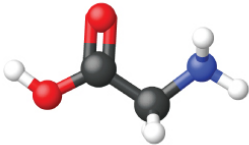
**Solution**

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in [\[link\]](#):



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine,  $\text{C}_2\text{H}_5\text{O}_2\text{N}$ , contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

**Equation:**

$$28.35 \text{ g glycine} \left( \frac{\text{mol glycine}}{75.07 \text{ g}} \right) = 0.378 \text{ mol glycine}$$

This result is consistent with our rough estimate.

### Check Your Learning

How many moles of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , are in a 25-g sample of sucrose?

**Note:**

**Answer:**

0.073 mol

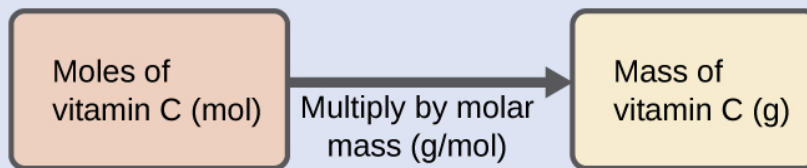
### Example:

#### Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula  $\text{C}_6\text{H}_8\text{O}_6$ . The recommended daily dietary allowance of vitamin C for children aged 4–8 years is  $1.42 \times 10^{-4}$  mol. What is the mass of this allowance in grams?

#### Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole ( $\sim 10^{-4}$  or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass ( $\sim 0.02$  g). Performing the calculation, we get:

**Equation:**

$$1.42 \times 10^{-4} \text{ mol vitamin C} \left( \frac{176.124 \text{ g}}{\text{mol vitamin C}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

**Check Your Learning**

What is the mass of 0.443 mol of hydrazine,  $\text{N}_2\text{H}_4$ ?

**Note:**

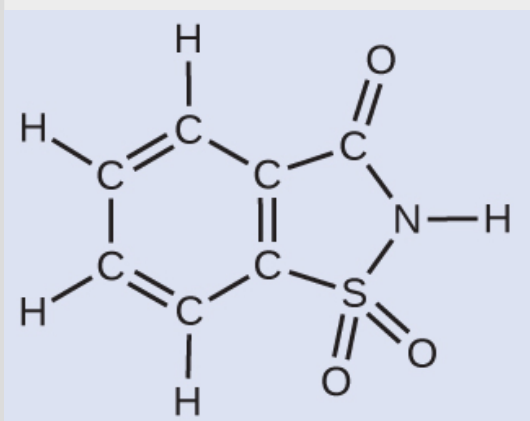
**Answer:**

14.2 g

**Example:**

**Deriving the Number of Atoms and Molecules from the Mass of a Compound**

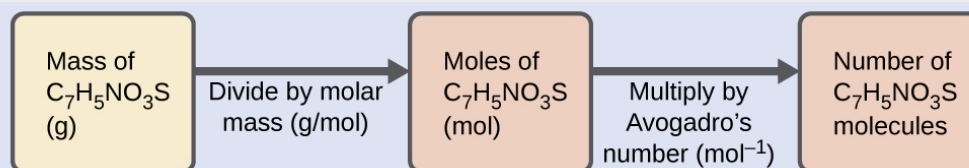
A packet of an artificial sweetener contains 40.0 mg of saccharin ( $\text{C}_7\text{H}_5\text{NO}_3\text{S}$ ), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

**Solution**

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in [\[link\]](#), and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

**Equation:**

$$0.0400 \text{ g C}_7\text{H}_5\text{NO}_3\text{S} \left( \frac{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}}{183.18 \text{ g C}_7\text{H}_5\text{NO}_3\text{S}} \right) \left( \frac{6.022 \times 10^{23} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}}{1 \text{ mol C}_7\text{H}_5\text{NO}_3\text{S}} \right) = 1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

**Equation:**

$$1.31 \times 10^{20} \text{ C}_7\text{H}_5\text{NO}_3\text{S molecules} \left( \frac{7 \text{ C atoms}}{1 \text{ C}_7\text{H}_5\text{NO}_3\text{S molecule}} \right) = 9.17 \times 10^{20} \text{ C atoms}$$

**Check Your Learning**

How many  $\text{C}_4\text{H}_{10}$  molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

**Note:**

**Answer:**

$9.545 \times 10^{22}$  molecules  $\text{C}_4\text{H}_{10}$ ;  $9.545 \times 10^{23}$  atoms H

**Note:**

**Counting Neurotransmitter Molecules in the Brain**

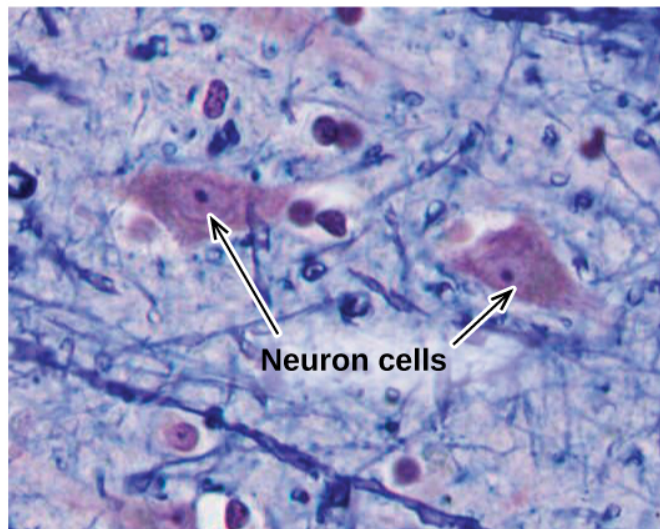
The brain is the control center of the central nervous system ([\[link\]](#)). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions;



it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies (more details available at [www.whitehouse.gov/share/brain-initiative](http://www.whitehouse.gov/share/brain-initiative)).



(a)

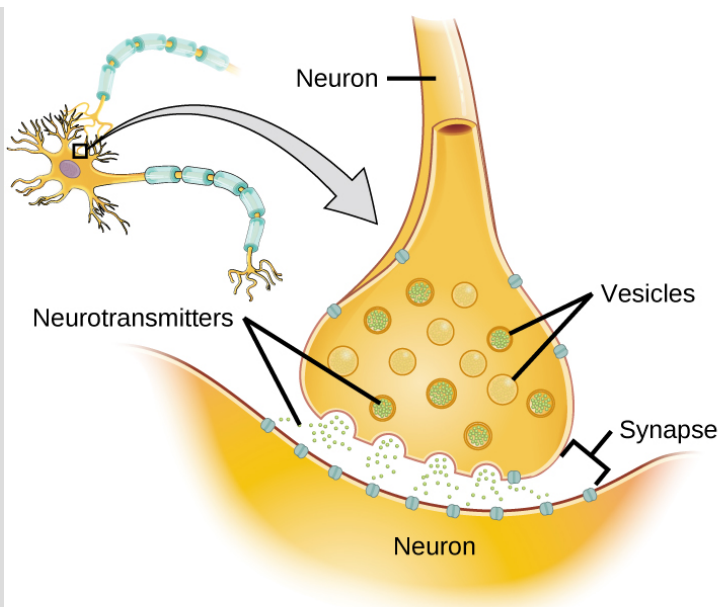


(b)

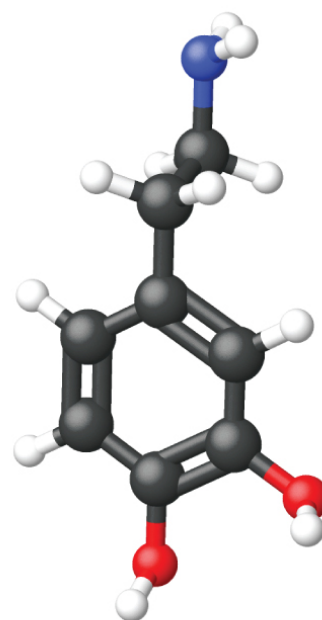
(a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L.

(b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse) and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell wall and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see [\[link\]](#)). One neurotransmitter that has been very extensively studied is dopamine,  $C_8H_{11}NO_2$ . Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.



(a)



(b)

(a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine,  $C_8H_{11}NO_2$ , is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle (about  $5 \times 10^{-20}$  mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.[\[footnote\]](#)

Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

## Key Concepts and Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be  $6.022 \times 10^{23}$ , a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

---

#### Solution:

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O<sub>2</sub>, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

### Exercise:

#### Problem:

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

### Exercise:

**Problem:** Write the molecular and empirical formulas of the following compounds:

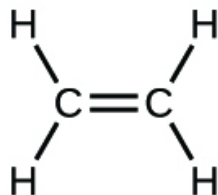
(a)



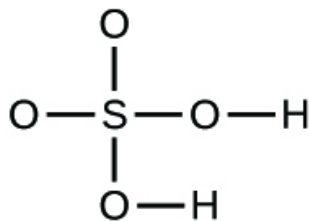
(b)



(c)



(d)



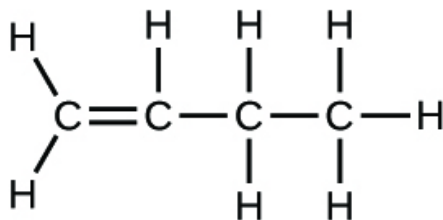
**Solution:**

(a) molecular  $\text{CO}_2$ , empirical  $\text{CO}_2$ ; (b) molecular  $\text{C}_2\text{H}_2$ , empirical  $\text{CH}$ ; (c) molecular  $\text{C}_2\text{H}_4$ , empirical  $\text{CH}_2$ ; (d) molecular  $\text{H}_2\text{SO}_4$ , empirical  $\text{H}_2\text{SO}_4$

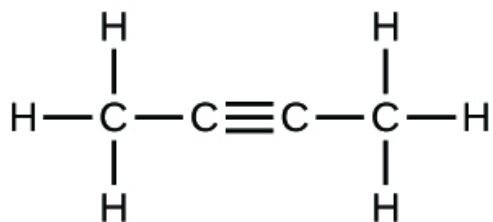
**Exercise:**

**Problem:** Write the molecular and empirical formulas of the following compounds:

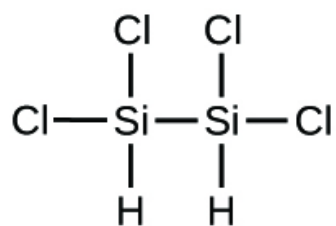
(a)



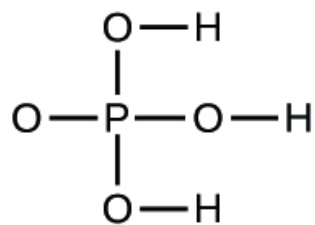
(b)



(c)



(d)



**Exercise:**

**Problem:** Determine the empirical formulas for the following compounds:

(a) caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$

(b) sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

(c) hydrogen peroxide,  $\text{H}_2\text{O}_2$

(d) glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$

(e) ascorbic acid (vitamin C),  $\text{C}_6\text{H}_8\text{O}_6$

---

**Solution:**

(a)  $\text{C}_4\text{H}_5\text{N}_2\text{O}$ ; (b)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ; (c)  $\text{HO}$ ; (d)  $\text{CH}_2\text{O}$ ; (e)  $\text{C}_3\text{H}_4\text{O}_3$

**Exercise:**

**Problem:** Determine the empirical formulas for the following compounds:

(a) acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$

(b) citric acid,  $\text{C}_6\text{H}_8\text{O}_7$

(c) hydrazine,  $\text{N}_2\text{H}_4$

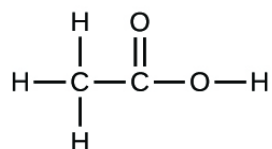
(d) nicotine,  $\text{C}_{10}\text{H}_{14}\text{N}_2$

(e) butane,  $\text{C}_4\text{H}_{10}$

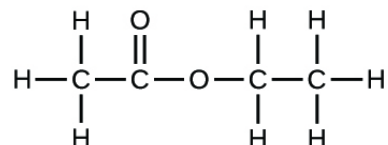
**Exercise:**

**Problem:** Write the empirical formulas for the following compounds:

(a)



(b)



---

**Solution:**

(a)  $\text{CH}_2\text{O}$ ; (b)  $\text{C}_2\text{H}_4\text{O}$

**Exercise:**

**Problem:**

Open the [Build a Molecule simulation](#) and select the “Larger Molecules” tab. Select an appropriate atom's “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

- (a) Draw the structural formula of this molecule and state its name.
- (b) Can you arrange these atoms in any way to make a different compound?

**Exercise:****Problem:**

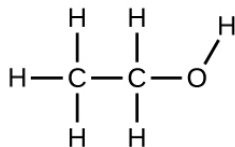
Use the [Build a Molecule simulation](#) to repeat [\[link\]](#), but build a molecule with two carbons, six hydrogens, and one oxygen.

- (a) Draw the structural formula of this molecule and state its name.
- (b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
- (c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

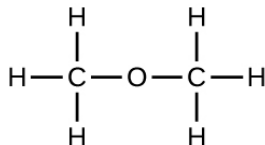
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**Solution:**

- (a) ethanol



- (b) methoxymethane, more commonly known as dimethyl ether



- (c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

**Exercise:**

**Problem:**

Use the [Build a Molecule simulation](#) to repeat [\[link\]](#), but build a molecule with three carbons, seven hydrogens, and one chlorine.

- (a) Draw the structural formula of this molecule and state its name.
- (b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
- (c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

**Exercise:****Problem:**

Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

---

**Solution:**

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

**Exercise:**

**Problem:** Compare 1 mole of  $\text{H}_2$ , 1 mole of  $\text{O}_2$ , and 1 mole of  $\text{F}_2$ .

- (a) Which has the largest number of molecules? Explain why.
- (b) Which has the greatest mass? Explain why.

**Exercise:****Problem:**

Which contains the greatest mass of oxygen: 0.75 mol of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 0.60 mol of formic acid ( $\text{HCO}_2\text{H}$ ), or 1.0 mol of water ( $\text{H}_2\text{O}$ )? Explain why.

---

**Solution:**

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

**Exercise:**



**Problem:**

Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 1 mol of formic acid ( $\text{HCO}_2\text{H}$ ), or 1 mol of water ( $\text{H}_2\text{O}$ )? Explain why.

**Exercise:****Problem:**

How are the molecular mass and the molar mass of a compound similar and how are they different?

---

**Solution:**

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of  $6.022 \times 10^{23}$  molecules.

**Exercise:**

**Problem:** Calculate the molar mass of each of the following compounds:

- (a) hydrogen fluoride,  $\text{HF}$
- (b) ammonia,  $\text{NH}_3$
- (c) nitric acid,  $\text{HNO}_3$
- (d) silver sulfate,  $\text{Ag}_2\text{SO}_4$
- (e) boric acid,  $\text{B}(\text{OH})_3$

**Exercise:**

**Problem:** Calculate the molar mass of each of the following:

- (a)  $\text{S}_8$
  - (b)  $\text{C}_5\text{H}_{12}$
  - (c)  $\text{Sc}_2(\text{SO}_4)_3$
  - (d)  $\text{CH}_3\text{COCH}_3$  (acetone)
  - (e)  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose)
- 

**Solution:**

(a) 256.528 g/mol; (b) 72.150 g mol<sup>-1</sup>; (c) 378.103 g mol<sup>-1</sup>; (d) 58.080 g mol<sup>-1</sup>; (e) 180.158 g mol<sup>-1</sup>

**Exercise:**

**Problem:**

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

- (a) limestone, CaCO<sub>3</sub>
- (b) halite, NaCl
- (c) beryl, Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>
- (d) malachite, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>
- (e) turquoise, CuAl<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub>

**Exercise:**

**Problem:** Calculate the molar mass of each of the following:

- (a) the anesthetic halothane, C<sub>2</sub>HBrClF<sub>3</sub>
- (b) the herbicide paraquat, C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>Cl<sub>2</sub>
- (c) caffeine, C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>
- (d) urea, CO(NH<sub>2</sub>)<sub>2</sub>
- (e) a typical soap, C<sub>17</sub>H<sub>35</sub>CO<sub>2</sub>Na

---

**Solution:**

(a) 197.382 g mol<sup>-1</sup>; (b) 257.163 g mol<sup>-1</sup>; (c) 194.193 g mol<sup>-1</sup>; (d) 60.056 g mol<sup>-1</sup>; (e) 306.464 g mol<sup>-1</sup>

**Exercise:**

**Problem:**

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

- (a) 25.0 g of propylene, C<sub>3</sub>H<sub>6</sub>
- (b)  $3.06 \times 10^{-3}$  g of the amino acid glycine, C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>

- (c) 25 lb of the herbicide Treflan,  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4\text{F}$  (1 lb = 454 g)
- (d) 0.125 kg of the insecticide Paris Green,  $\text{Cu}_4(\text{AsO}_3)_2(\text{CH}_3\text{CO}_2)_2$
- (e) 325 mg of aspirin,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2\text{CH}_3)$

**Exercise:**

**Problem:** Determine the mass of each of the following:

- (a) 0.0146 mol KOH
- (b) 10.2 mol ethane,  $\text{C}_2\text{H}_6$
- (c)  $1.6 \times 10^{-3}$  mol  $\text{Na}_2\text{SO}_4$
- (d)  $6.854 \times 10^3$  mol glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$
- (e) 2.86 mol  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$
- 

**Solution:**

- (a) 0.819 g;
- (b) 307 g;
- (c) 0.23 g;
- (d)  $1.235 \times 10^6$  g (1235 kg);
- (e) 765 g

**Exercise:**

**Problem:**

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

- (a) 2.12 g of potassium bromide, KBr
- (b) 0.1488 g of phosphoric acid,  $\text{H}_3\text{PO}_4$
- (c) 23 kg of calcium carbonate,  $\text{CaCO}_3$
- (d) 78.452 g of aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$
- (e) 0.1250 mg of caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$

**Exercise:**

**Problem:** Determine the mass of each of the following:

- (a) 2.345 mol LiCl
  - (b) 0.0872 mol acetylene,  $\text{C}_2\text{H}_2$
  - (c)  $3.3 \times 10^{-2}$  mol  $\text{Na}_2\text{CO}_3$
  - (d)  $1.23 \times 10^3$  mol fructose,  $\text{C}_6\text{H}_{12}\text{O}_6$
  - (e) 0.5758 mol  $\text{FeSO}_4(\text{H}_2\text{O})_7$
- 

**Solution:**

- (a) 99.41 g;
- (b) 2.27 g;
- (c) 3.5 g;
- (d) 222 kg;
- (e) 160.1 g

**Exercise:**

**Problem:**

The approximate minimum daily dietary requirement of the amino acid leucine,  $\text{C}_6\text{H}_{13}\text{NO}_2$ , is 1.1 g. What is this requirement in moles?

**Exercise:**

**Problem:** Determine the mass in grams of each of the following:

- (a) 0.600 mol of oxygen atoms
  - (b) 0.600 mol of oxygen molecules,  $\text{O}_2$
  - (c) 0.600 mol of ozone molecules,  $\text{O}_3$
- 

**Solution:**

- (a) 9.60 g; (b) 19.2 g; (c) 28.8 g

**Exercise:**

**Problem:**

A 55-kg woman has  $7.5 \times 10^{-3}$  mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

**Exercise:**

**Problem:**

Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon,  $\text{ZrSiO}_4$ , a semiprecious stone.

---

**Solution:**

zirconium:  $2.038 \times 10^{23}$  atoms; 30.87 g; silicon:  $2.038 \times 10^{23}$  atoms; 9.504 g; oxygen:  $8.151 \times 10^{23}$  atoms; 21.66 g

**Exercise:****Problem:**

Determine which of the following contains the greatest mass of hydrogen: 1 mol of  $\text{CH}_4$ , 0.6 mol of  $\text{C}_6\text{H}_6$ , or 0.4 mol of  $\text{C}_3\text{H}_8$ .

**Exercise:****Problem:**

Determine which of the following contains the greatest mass of aluminum: 122 g of  $\text{AlPO}_4$ , 266 g of  $\text{Al}_2\text{Cl}_6$ , or 225 g of  $\text{Al}_2\text{S}_3$ .

---

**Solution:**

$\text{AlPO}_4$ : 1.000 mol or 26.98 g Al

$\text{Al}_2\text{Cl}_6$ : 1.994 mol or 53.74 g Al

$\text{Al}_2\text{S}_3$ : 3.00 mol or 80.94 g Al

The  $\text{Al}_2\text{S}_3$  sample thus contains the greatest mass of Al.

**Exercise:****Problem:**

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

**Exercise:****Problem:**

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

---

**Solution:**

$3.113 \times 10^{25}$  C atoms

**Exercise:**

**Problem:**

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

**Exercise:****Problem:**

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose,  $C_{12}H_{22}O_{11}$ ) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

---

**Solution:**

0.865 servings, or about 1 serving.

**Exercise:****Problem:**

A tube of toothpaste contains 0.76 g of sodium monofluorophosphate ( $Na_2PO_3F$ ) in 100 mL.

(a) What mass of fluorine atoms in mg was present?

(b) How many fluorine atoms were present?

**Exercise:**

**Problem:** Which of the following represents the least number of molecules?

(a) 20.0 g of  $H_2O$  (18.02 g/mol)

(b) 77.0 g of  $CH_4$  (16.06 g/mol)

(c) 68.0 g of  $CaH_2$  (42.09 g/mol)

(d) 100.0 g of  $N_2O$  (44.02 g/mol)

(e) 84.0 g of  $HF$  (20.01 g/mol)

---

**Solution:**

20.0 g  $H_2O$  represents the least number of molecules since it has the least number of moles.

## Glossary

### empirical formula

formula showing the composition of a compound given as the simplest whole-number ratio of atoms

### isomers

compounds with the same chemical formula but different structures

### molecular formula

formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

### spatial isomers

compounds in which the relative orientations of the atoms in space differ

### structural formula

shows the atoms in a molecule and how they are connected

### structural isomer

one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

## Introduction

class="introduction"

- Electromagnetic Energy
- The Bohr Model
- Development of Quantum Theory
- Electronic Structure of Atoms (Electron Configurations)
- Periodic Variations in Element Properties

The Crab  
Nebula  
consists of  
remnants of a  
supernova  
(the explosion  
of a star).

NASA's  
Hubble Space  
Telescope  
produced this  
composite  
image.

Measurements of the  
emitted light  
wavelengths  
enabled  
astronomers  
to identify the  
elements in  
the nebula,  
determining  
that it  
contains  
specific ions  
including  $S^+$



(green  
filaments) and  
 $O^{2+}$  (red  
filaments).

(credit:  
modification  
of work by  
NASA and  
ESA)



In 1054, Chinese astronomers recorded the appearance of a “guest star” in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula ([\[link\]](#)) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

## Basics of Electromagnetic Energy

By the end of this section, you will be able to:

- Explain the basic behavior of waves, including travelling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this

framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

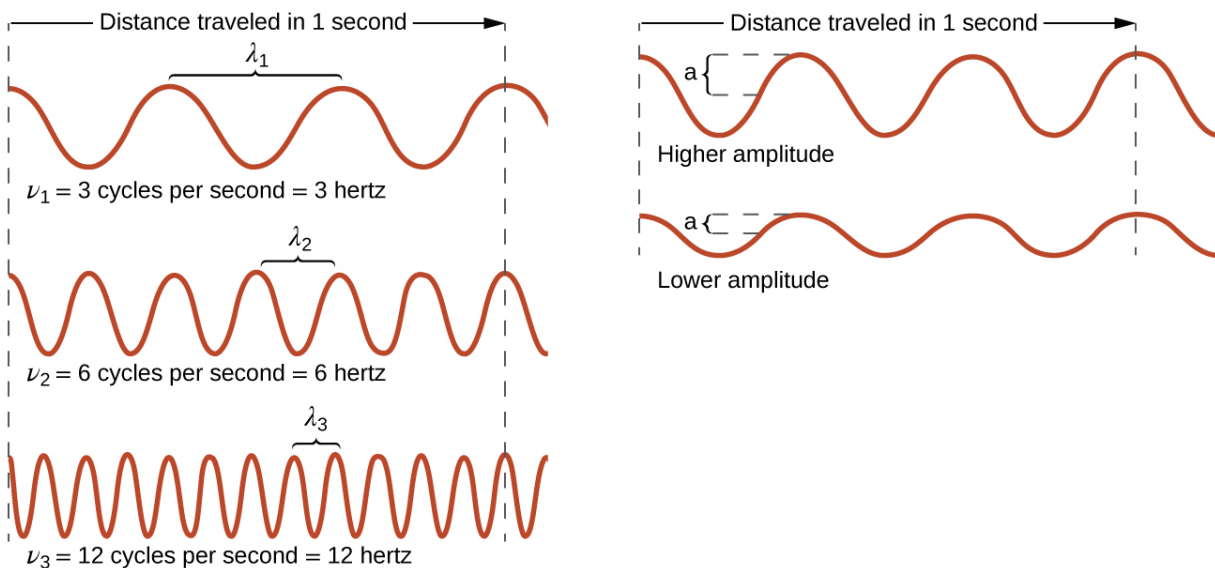
## Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave—they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the

direction of travel. These waves can travel through a vacuum at a constant speed of  $2.998 \times 10^8$  m/s, the speed of light (denoted by  $c$ ).

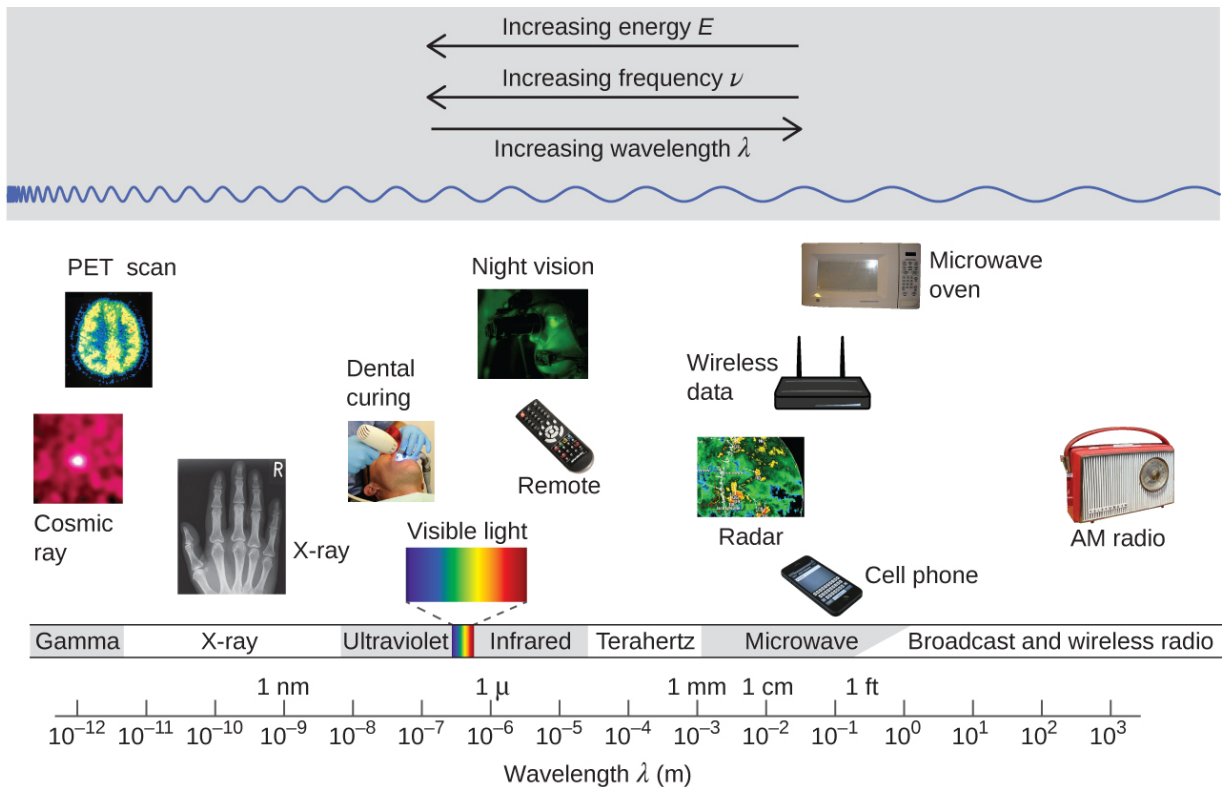
All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by  $\lambda$ , the lowercase Greek letter lambda), a **frequency** (denoted by  $\nu$ , the lowercase Greek letter nu), and an **amplitude**. As can be seen in [\[link\]](#), the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers ( $10^3$  m) to picometers ( $10^{-12}$  m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [ $s^{-1}$ ], is the **hertz (Hz)**. Common multiples of this unit are megahertz, ( $1 \text{ MHz} = 1 \times 10^6 \text{ Hz}$ ) and gigahertz ( $1 \text{ GHz} = 1 \times 10^9 \text{ Hz}$ ). The amplitude corresponds to the magnitude of the wave's displacement and so, in [\[link\]](#), this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.



One-dimensional sinusoidal waves show the relationship among

wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in [\[link\]](#). This figure also shows the **electromagnetic spectrum**, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).



Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit “Cosmic ray”: modification of work by NASA; credit “PET scan”: modification of work by the National Institute of Health; credit “X-ray”: modification of work by Dr. Jochen Lengerke; credit “Dental curing”: modification of work by the Department of the Navy; credit “Night vision”: modification of work by the Department of the Army; credit “Remote”: modification of work by Emilian Robert Vicol; credit “Cell phone”: modification of work by Brett Jordan; credit “Microwave oven”: modification of work by Billy Mabray; credit “Ultrasound”: modification of work by Jane Whitney; credit “AM radio”: modification of work by Dave Clausen)

**Note:**  
Dorothy Hodgkin



Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin. She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B<sub>12</sub>, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

## Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in [\[link\]](#), sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to

the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in [\[link\]](#).

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in [\[link\]](#). Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way ([\[link\]](#)). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.

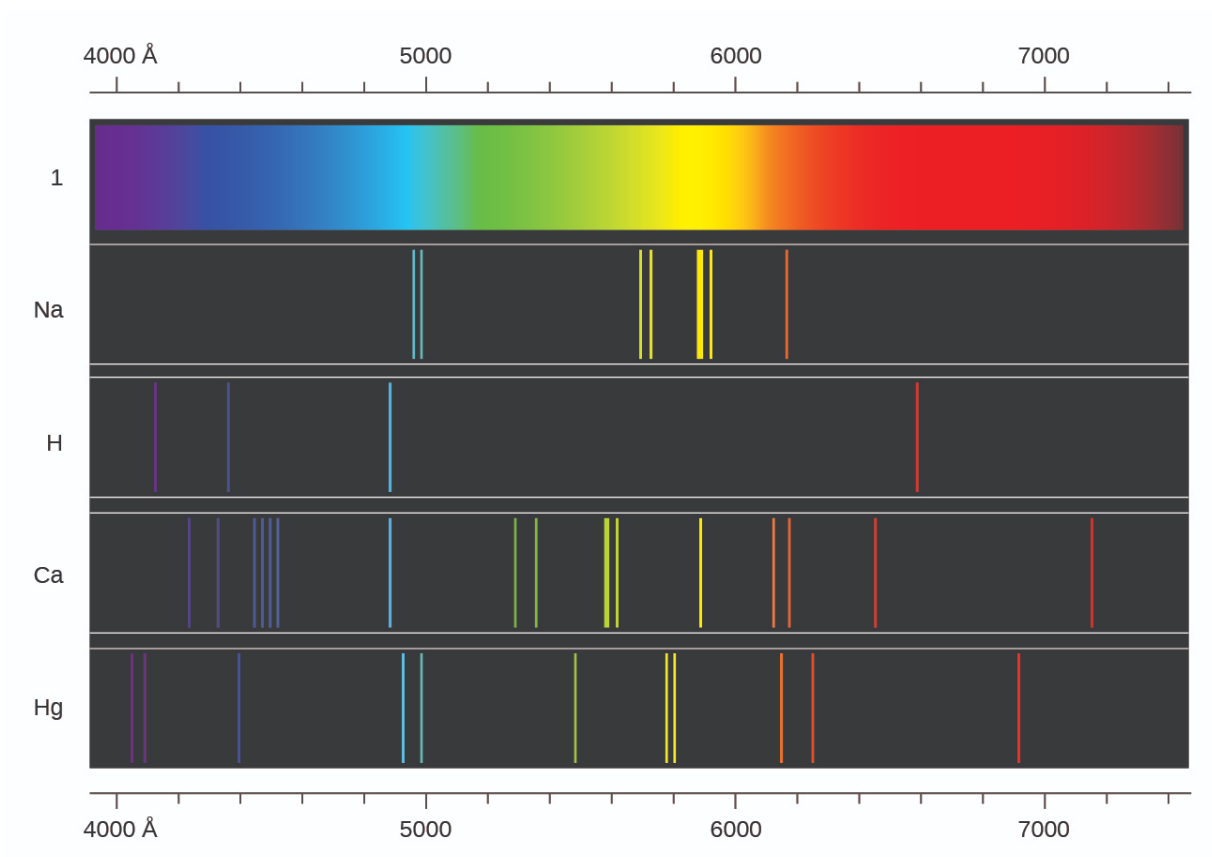


Neon signs operate by exciting a gas at low partial pressure using an



electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the  $\text{H}_2$  molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in [\[link\]](#).



Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers.

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

## **Key Concepts and Summary**

Electromagnetic radiation helps to show us that there are only very specific energy levels within an atom. This will allow us to look more closely at the electronic structure in the next section of this book.

## **Glossary**

amplitude

extent of the displacement caused by a wave

blackbody

idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

continuous spectrum

electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation

energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum

range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays

endothermic

processes that increase the energy of an atom and involve the absorption of light

exothermic

processes that decrease the energy of an atom and involve the emission of light

frequency ( $\nu$ )

number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)

the unit of frequency, which is the number of cycles per second,  $s^{-1}$

intensity

property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern

pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum

electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node

any point of a standing wave with zero amplitude

photon

smallest possible packet of electromagnetic radiation, a particle of light

quantization

limitation of some property to specific discrete values, not continuous

standing wave

(also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

wave

oscillation of a property over time or space; can transport energy from one point to another

wavelength ( $\lambda$ )

distance between two consecutive peaks or troughs in a wave

wave-particle duality

observation that elementary particles can exhibit both wave-like and particle-like properties

## Electronic Structure of Atoms (Electron Configurations)

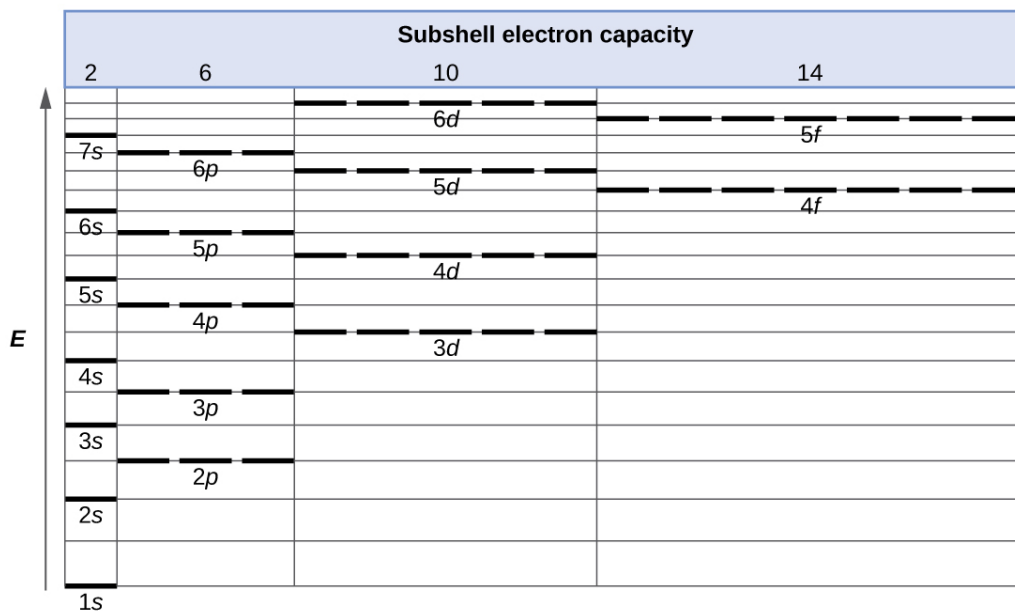
By the end of this section, you will be able to:

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

## Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number,  $n$ , increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of  $l$  differ so that the energy of the orbitals increases within a shell in the order  $s < p < d < f$ . [\[link\]](#) depicts how these two trends in increasing energy relate. The  $1s$  orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the  $2s$  and then  $2p$ ,  $3s$ , and  $3p$  orbitals, showing that the increasing  $n$  value has more influence on energy than the increasing  $l$  value for small atoms. However, this pattern does not hold for larger atoms. The  $3d$  orbital is higher in energy than the  $4s$  orbital. Such overlaps continue to occur frequently as we move up the chart.



Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

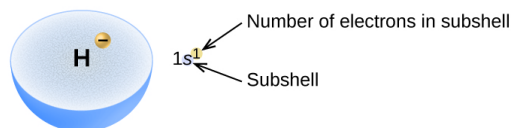
Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the  $5p$  orbitals fill immediately after the  $4d$ , and immediately before the  $6s$ . The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number,  $n$ , increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of  $l$  increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order  $s > p > d > f$ . Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have  $-1$  charges, but nuclei have  $+Z$  charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals ( $1s$

through  $3p$ ), the increase in energy due to  $n$  is more significant than the increase due to  $l$ ; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information ([link](#)):

1. The number of the principal quantum shell,  $n$ ,
2. The letter that designates the orbital type (the subshell,  $l$ ), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation  $2p^4$  (read "two-p-four") indicates four electrons in a  $p$  subshell ( $l = 1$ ) with a principal quantum number ( $n$ ) of 2. The notation  $3d^8$  (read "three-d-eight") indicates eight electrons in the  $d$  subshell (i.e.,  $l = 2$ ) of the principal shell for which  $n = 3$ .

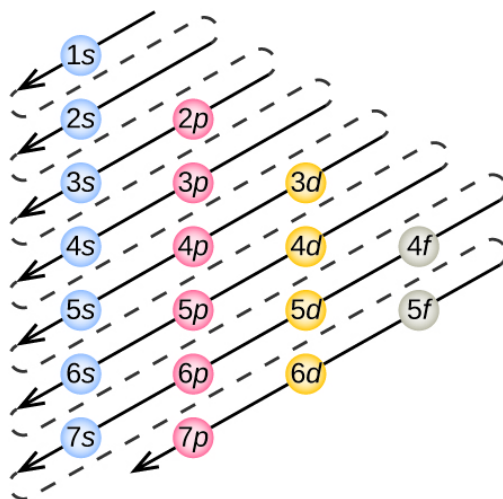


The diagram of an electron configuration specifies the subshell ( $n$  and  $l$  value, with letter symbol) and superscript number of electrons.

## The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau*

(“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in [\[link\]](#)), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. [\[link\]](#) illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, [\[link\]](#) provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing  $Z$  order. For example, after filling the  $3p$  block up to Ar, we see the orbital will be  $4s$  (K, Ca), followed by the  $3d$  orbitals.

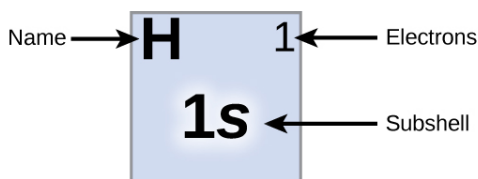


This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.



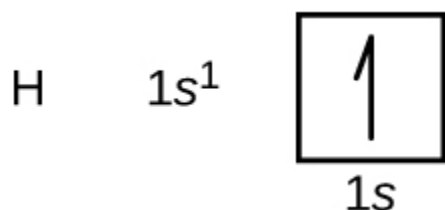
**Electron Configuration Table**

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		H 1 1s																	He 2 1s
2		Li 1 2s	Be 2 2s											B 1 2p	C 2 2p	N 3 2p	O 4 2p	F 5 2p	Ne 6 2p
3		Na 1 3s	Mg 2 3s											Al 1 3p	Si 2 3p	P 3 3p	S 4 3p	Cl 5 3p	Ar 6 3p
4		K 1 4s	Ca 2 4s	Sc 1 3d	Ti 2 3d	V 3 3d	Cr 4 3d	Mn 5 3d	Fe 6 3d	Co 7 3d	Ni 8 3d	Cu 9 3d	Zn 10 3d	Ga 1 4p	Ge 2 4p	As 3 4p	Se 4 4p	Br 5 4p	Kr 6 4p
5		Rb 1 5s	Sr 2 5s	Y 1 4d	Zr 2 4d	Nb 3 4d	Mo 4 4d	Tc 5 4d	Ru 6 4d	Rh 7 4d	Pd 8 4d	Ag 9 4d	Cd 10 4d	In 1 5p	Sn 2 5p	Sb 3 5p	Te 4 5p	I 5 5p	Xe 6 5p
6		Cs 1 6s	Ba 2 6s	La *1 5d	Hf 2 5d	Ta 3 5d	W 4 5d	Re 5 5d	Os 6 5d	Ir 7 5d	Pt 8 5d	Au 9 5d	Hg 10 5d	Tl 1 6p	Pb 2 6p	Bi 3 6p	Po 4 6p	At 5 6p	Rn 6 6p
7		Fr 1 7s	Ra 2 7s	Ac **1 6d	Rf 2 6d	Db 3 6d	Sg 4 6d	Bh 5 6d	Hs 6 6d	Mt 7 6d	Ds 8 6d	Rg 9 6d	Cn 10 6d	Nh 1 7p	Fl 2 7p	Mc 3 7p	Lv 4 7p	Ts 5 7p	Og 6 7p
				* Ce 1 4f	Pr 2 4f	Nd 3 4f	Pm 4 4f	Sm 5 4f	Eu 6 4f	Gd 7 4f	Tb 8 4f	Dy 9 4f	Ho 10 4f	Er 11 4f	Tm 12 4f	Yb 13 4f	Lu 14 4f		
				** Th 1 5f	Pa 2 5f	U 3 5f	Np 4 5f	Pu 5 5f	Am 6 5f	Cm 7 5f	Bk 8 5f	Cf 9 5f	Es 10 5f	Fm 11 5f	Md 12 5f	No 13 5f	Lr 14 5f		

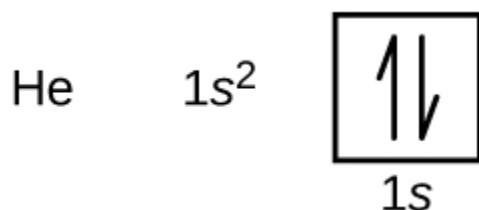


This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to [\[link\]](#) or [\[link\]](#), we would expect to find the electron in the 1s orbital. By convention, the  $m_s = +\frac{1}{2}$  value is usually filled first. The electron configuration and the orbital diagram are:

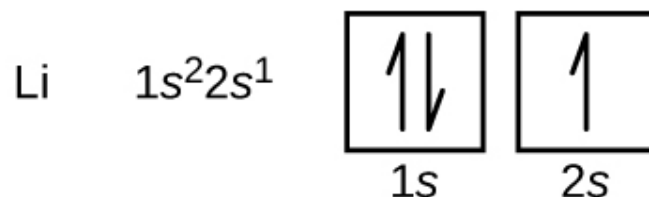


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ( $n = 1$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = +\frac{1}{2}$ ). The second electron also goes into the 1s orbital and fills that orbital. The second electron has the same  $n$ ,  $l$ , and  $m_l$  quantum numbers, but must have the opposite spin quantum number,  $m_s = -\frac{1}{2}$ . This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

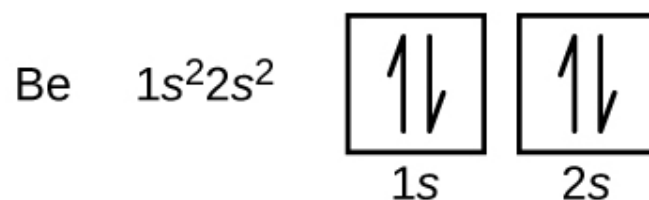


The  $n = 1$  shell is completely filled in a helium atom.

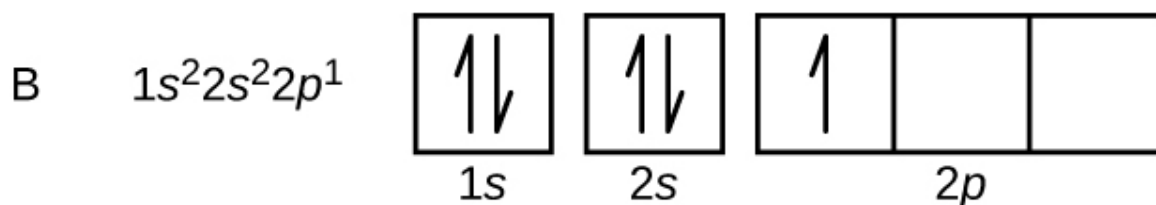
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital ([\[link\]](#) or [\[link\]](#)). Thus, the electron configuration and orbital diagram of lithium are:



An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.

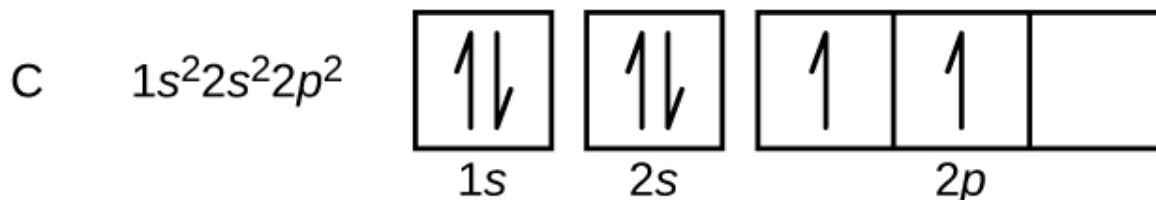


An atom of boron (atomic number 5) contains five electrons. The  $n = 1$  shell is filled with two electrons and three electrons will occupy the  $n = 2$  shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2p orbital. There are three degenerate 2p orbitals ( $m_l = -1, 0, +1$ ) and the electron can occupy any one of these p orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

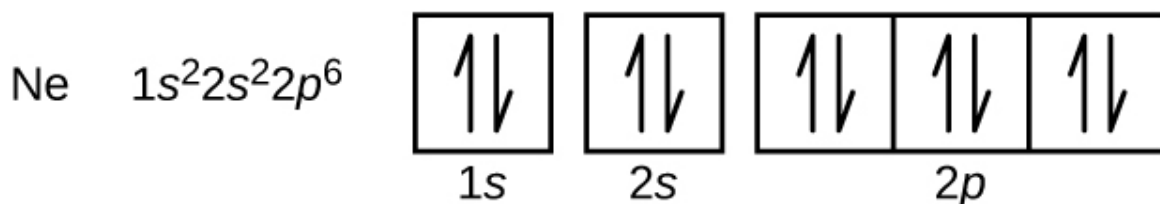
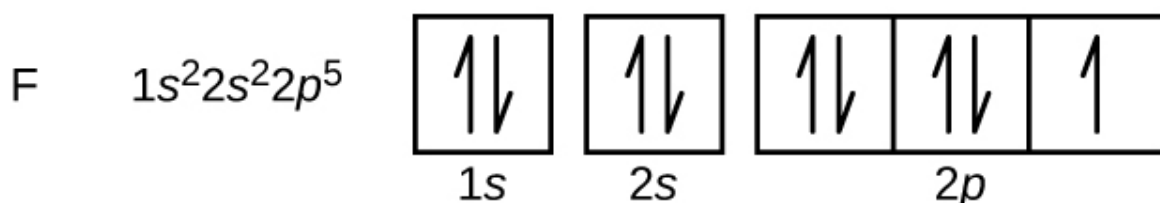
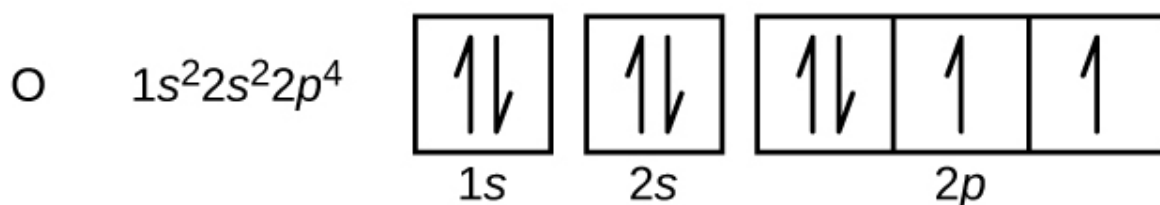
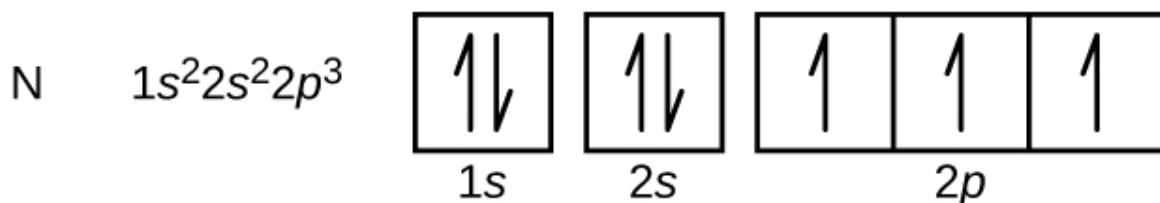


Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2p subshell. We now have a choice of filling one of the 2p orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, p orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2p orbitals have identical  $n$ ,  $l$ , and  $m_s$  quantum

numbers and differ in their  $m_l$  quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

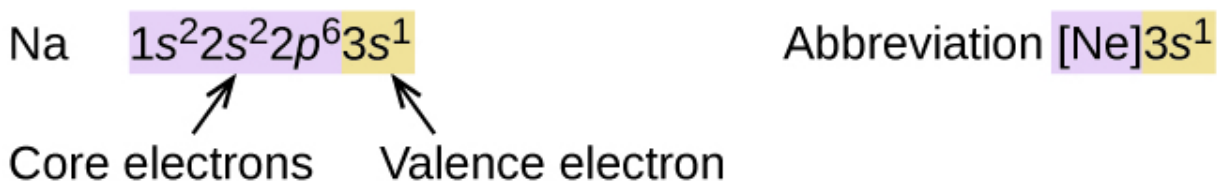


Nitrogen (atomic number 7) fills the  $1s$  and  $2s$  subshells and has one electron in each of the three  $2p$  orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the  $2p$  orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one  $2p$  orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the  $n = 1$  and the  $n = 2$  shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a  $1s^2 2s^2 2p^6 3s^1$  configuration. The electrons occupying the outermost shell orbital(s) (highest value of  $n$ ) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** ([\[link\]](#)). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example,

the symbol [Ne] represents core electrons, ( $1s^2 2s^2 2p^6$ ) and our abbreviated or condensed configuration is  $[\text{Ne}]3s^1$ .



A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as  $[\text{He}]2s^1$ , where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence s subshell outside a filled set of inner shells.

**Equation:**



The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a  $[\text{Ne}]3s^2$  configuration, is analogous to its family member beryllium,  $[\text{He}]2s^2$ . Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration  $[\text{Ne}]3s^2 3p^1$ , is analogous to its family member boron,  $[\text{He}]2s^2 2p^1$ .

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18

electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to  $n = 3$ . [\[link\]](#) shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

Period

Group

Electron Configuration Table

1	1	H																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														</
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Atomic number	→ 1	<b>H</b>	← Name
		1s <sup>1</sup>	← Outer electron configuration

This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the  $3d$  subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the  $3d$  level but is, instead, added to the  $4s$  level ([\[link\]](#)). As discussed previously, the  $3d$  orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the  $4s$ , which has three radial nodes. Thus, potassium has an electron configuration of  $[\text{Ar}]4s^1$ . Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the  $4s$  subshell and calcium has an electron configuration of  $[\text{Ar}]4s^2$ . This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the  $3d$  subshell. This subshell is filled to its capacity with 10 electrons (remember that for  $l = 2$  [ $d$  orbitals], there are  $2l + 1 = 5$  values of  $m_l$ , meaning that there are five  $d$  orbitals that have a combined capacity of 10 electrons). The  $4p$  subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10  $d$  electrons are successively added to the  $(n - 1)$  shell next to the  $n$  shell to bring that  $(n - 1)$  shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14  $f$  electrons ( $l = 3$ ,  $2l + 1 = 7$   $m_l$  values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the  $(n - 2)$  shell to bring that shell from 18 electrons to a total of 32 electrons.

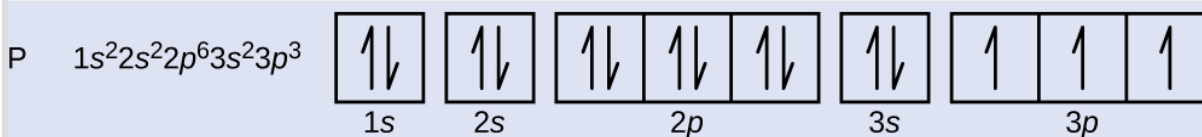
**Example:****Quantum Numbers and Electron Configurations**

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

**Solution**



The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $4s$ , . . . The 15 electrons of the phosphorus atom will fill up to the  $3p$  orbital, which will contain three electrons:



The last electron added is a  $3p$  electron. Therefore,  $n = 3$  and, for a  $p$ -type orbital,  $l = 1$ . The  $m_l$  value could be  $-1$ ,  $0$ , or  $+1$ . The three  $p$  orbitals are degenerate, so any of these  $m_l$  values is correct. For unpaired electrons, convention assigns the value of  $+\frac{1}{2}$  for the spin quantum number; thus,  $m_s = +\frac{1}{2}$ .

### Check Your Learning

Identify the atoms from the electron configurations given:

(a)  $[\text{Ar}]4s^2 3d^5$

(b)  $[\text{Kr}]5s^2 4d^{10} 5p^6$

### Note:

### Answer:

(a) Mn (b) Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in [\[link\]](#) or [\[link\]](#). For instance, the electron configurations (shown in [\[link\]](#)) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4s into the 3d orbital to gain the extra stability of a half-filled 3d subshell (in Cr) or a filled 3d subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration  $[\text{Kr}]5s^24d^3$ . Experimentally, we observe that its ground-state electron configuration is actually  $[\text{Kr}]5s^14d^4$ . We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5s orbital are larger than the gap in energy between the 5s and 4d orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

## Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table ([link](#)), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their

atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in [\[link\]](#), which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of [\[link\]](#) show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an  $s$  or a  $p$  orbital in the outermost shell, shown in blue and red in [\[link\]](#). This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest  $n$  level. For example, gallium (Ga, atomic number 31) has the electron configuration  $[\text{Ar}]4s^23d^{10}\underline{4p^1}$ , which contains three valence electrons (underlined). The completely filled  $d$  orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals.** These are metallic elements in which the last electron added enters a  $d$  orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the  $ns$  and  $(n - 1) d$  electrons. The official IUPAC definition of transition elements specifies those with partially filled  $d$  orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in [\[link\]](#)) are not technically transition elements. However, the term is frequently used to refer to the entire  $d$  block (colored yellow in [\[link\]](#)), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an  $f$  orbital. They are shown in green in [\[link\]](#). The valence shells of the inner transition elements consist of the  $(n - 2)f$ , the  $(n - 1)d$ , and the  $ns$  subshells. There are two inner transition series:
  - a. The lanthanide series: lanthanide (La) through lutetium (Lu)
  - b. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

## Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the  $(n - 1)d$  or  $(n - 2)f$  electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

### Example:

#### Predicting Electron Configurations of Ions

What is the electron configuration of:

- (a)  $\text{Na}^+$
- (b)  $\text{P}^{3-}$
- (c)  $\text{Al}^{2+}$
- (d)  $\text{Fe}^{2+}$
- (e)  $\text{Sm}^{3+}$

#### Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

(a) Na:  $1s^2 2s^2 2p^6 3s^1$ . Sodium cation loses one electron, so  $\text{Na}^+$ :  
 $1s^2 2s^2 2p^6 3s^1 = \text{Na}^+ : 1s^2 2s^2 2p^6$ .

(b) P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ . Phosphorus trianion gains three electrons, so  $P^{3-}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

(c) Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$ . Aluminum dication loses two electrons  $Al^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^1 =$   
 $Al^{2+}$ :  $1s^2 2s^2 2p^6 3s^1$ .

(d) Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital  $Fe^{2+}$ :

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ .

(e). Sm:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$ . Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4f orbital.  $Sm^{3+}$ :

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 =$

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$ .

### Check Your Learning

Which ion with a +2 charge has the electron configuration

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$ ? Which ion with a +3 charge has this configuration?

### Note:

### Answer:

$Tc^{2+}$ ,  $Ru^{3+}$

## Key Concepts and Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

### Exercise:

#### Problem:

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

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#### Solution:

For example,  $\text{Na}^+$ :  $1s^2 2s^2 2p^6$ ;  $\text{Ca}^{2+}$ :  $1s^2 2s^2 2p^6$ ;  $\text{Sn}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$ ;  $\text{F}^-$ :  $1s^2 2s^2 2p^6$ ;  $\text{O}^{2-}$ :  $1s^2 2s^2 2p^6$ ;  $\text{Cl}^-$ :  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

### Exercise:

**Problem:**

Using complete subshell notation (not abbreviations,  $1s^2 2s^2 2p^6$ , and so forth), predict the electron configuration of each of the following atoms:

- (a) C
- (b) P
- (c) V
- (d) Sb
- (e) Sm

**Exercise:****Problem:**

Using complete subshell notation ( $1s^2 2s^2 2p^6$ , and so forth), predict the electron configuration of each of the following atoms:

- (a) N
- (b) Si
- (c) Fe
- (d) Te
- (e) Tb

---

**Solution:**

(a)  $1s^2 2s^2 2p^3$ ; (b)  $1s^2 2s^2 2p^6 3s^2 3p^2$ ; (c)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ ; (d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$ ; (e)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

**Exercise:**

**Problem:**

Is  $1s^2 2s^2 2p^6$  the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

**Exercise:****Problem:**

What additional information do we need to answer the question “Which ion has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$ ”?

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**Solution:**

The charge on the ion.

**Exercise:****Problem:**

Draw the orbital diagram for the valence shell of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Ru

**Exercise:****Problem:**

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

(a) N



(b) Si

(c) Fe

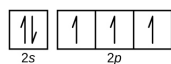
(d) Te

(e) Mo

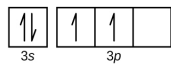
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**Solution:**

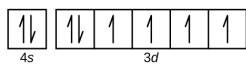
(a)



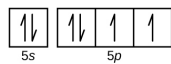
(b)



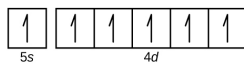
(c)



(d)



(e)



**Exercise:**

**Problem:**

Using complete subshell notation ( $1s^2 2s^2 2p^6$ , and so forth), predict the electron configurations of the following ions.

(a)  $N^{3-}$

(b)  $Ca^{2+}$

(c)  $S^-$

(d)  $Cs^{2+}$

(e)  $Cr^{2+}$

(f)  $Gd^{3+}$

**Exercise:****Problem:**

Which atom has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$ ?

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**Solution:**

Zr

**Exercise:****Problem:**

Which atom has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$ ?

**Exercise:****Problem:**

Which ion with a +1 charge has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ? Which ion with a -2 charge has this configuration?

---

**Solution:**



**Exercise:**

**Problem:**

Which of the following atoms contains only three valence electrons:  
Li, B, N, F, Ne?

**Exercise:**

**Problem:** Which of the following has two unpaired electrons?

- (a) Mg
  - (b) Si
  - (c) S
  - (d) Both Mg and S
  - (e) Both Si and S.
- 

**Solution:**

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

**Exercise:**

**Problem:**

Which atom would be expected to have a half-filled  $6p$  subshell?

**Exercise:**

**Problem:**

Which atom would be expected to have a half-filled  $4s$  subshell?

---

**Solution:**

K

**Exercise:****Problem:**

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ . Write the electron structure of the two cations.

**Exercise:****Problem:**

Thallium was used as a poison in the Agatha Christie mystery story "The Pale Horse." Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

---

**Solution:**

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^{14} 5d^{10}$

**Exercise:****Problem:**

Write the electron configurations for the following atoms or ions:

(a)  $\text{B}^{3+}$

(b)  $\text{O}^-$

(c)  $\text{Cl}^{3+}$

(d)  $\text{Ca}^{2+}$

(e) Ti

**Exercise:****Problem:**

Cobalt-60 and iodine-131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

---

**Solution:**

Co has 27 protons, 27 electrons, and 33 neutrons:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ . I has 53 protons, 53 electrons, and 78 neutrons:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$ .

**Exercise:****Problem:**

Write a set of quantum numbers for each of the electrons with an  $n$  of 3 in a Sc atom.

**Glossary****Aufbau principle**

procedure in which the electron configuration of the elements is determined by “building” them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

**core electron**

electron in an atom that occupies the orbitals of the inner shells

**electron configuration**

listing that identifies the electron occupancy of an atom’s shells and subshells

**Hund’s rule**

every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied

orbitals have the same spin

orbital diagram

pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

valence electrons

electrons in the outermost or valence shell (highest value of  $n$ ) of a ground-state atom

valence shell

outermost shell of electrons in a ground-state atom

## Periodic Variations in Element Properties

By the end of this section, you will be able to:

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

### Note:

Explore [visualizations](#) of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

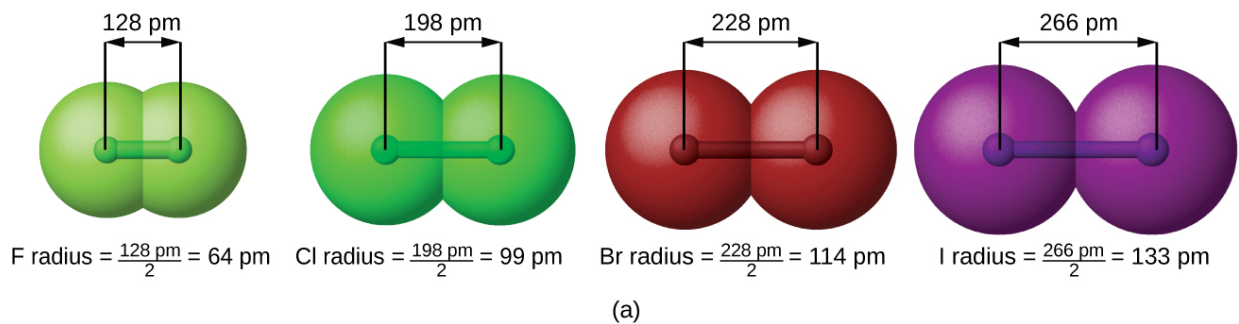
## Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** ([link](#)), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number,  $n$ , increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in [link](#) and [link](#). The trends for the entire periodic table can be seen in [link](#).

### Covalent Radii of the Halogen Group Elements

Atomic Radii of the Halogens (pm)	Nuclear charge
-----------------------------------	----------------

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85



Periodic Table of the Elements

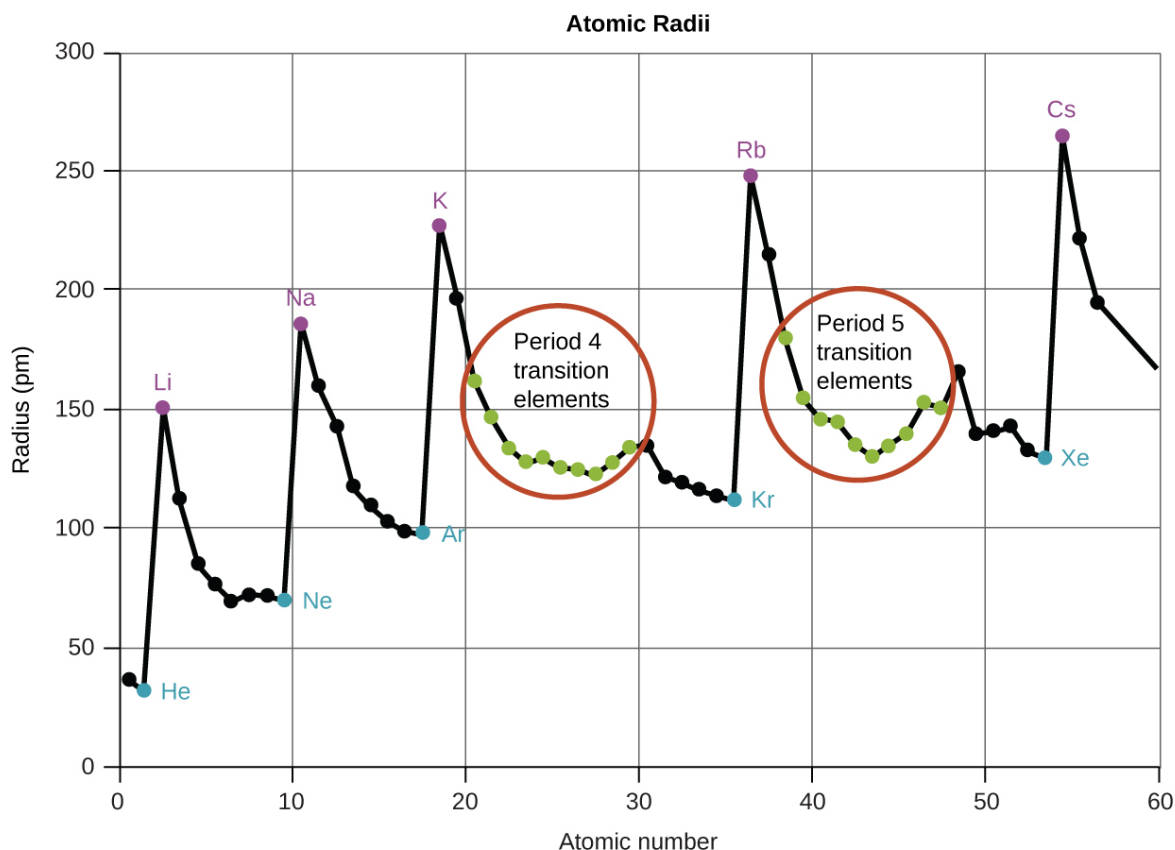
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

(b)

(a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule



consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as  $n$  increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.



Within each period, the trend in atomic radius decreases as  $Z$  increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as  $Z$  increases.

As shown in [\[link\]](#), as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge,  $Z_{\text{eff}}$** . This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge ( $Z$ ) and the effective nuclear charge ( $Z_{\text{eff}}$ ) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

**Equation:**

$$Z_{\text{eff}} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period,  $Z$  increases by one, but the shielding increases only slightly. Thus,  $Z_{\text{eff}}$  increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the  $ns$  or  $np$  electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the  $ns$  electrons before they begin to lose the  $(n - 1)d$  electrons, even though the  $ns$  electrons are added first, according to the Aufbau principle.

#### **Example:**

##### **Sorting Atomic Radii**

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

##### **Solution**

Radius increases as we move down a group, so  $\text{Ge} < \text{Fl}$  (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so  $\text{Kr} < \text{Br} < \text{Ge}$ . Putting the trends together, we obtain  $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$ .

##### **Check Your Learning**

Give an example of an atom whose size is smaller than fluorine.

#### **Note:**

##### **Answer:**

Ne or He

## **Variation in Ionic Radii**

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived ([link](#)). For example, the covalent radius of an aluminum atom ( $1s^2 2s^2 2p^6 3s^2 3p^1$ ) is 118 pm, whereas the ionic radius of an  $\text{Al}^{3+}$  ( $1s^2 2s^2 2p^6$ ) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge  $Z_{\text{eff}}$  (as discussed) and are drawn even closer to the nucleus.

 Al 118	 S 104
 Al <sup>3+</sup> 68	 S <sup>2-</sup> 170

The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V<sup>2+</sup> has an ionic radius of 79 pm, while that of V<sup>3+</sup> is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number,  $n$ .

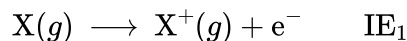
An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in  $Z_{\text{eff}}$  per electron. Both effects (the increased number of electrons and the decreased  $Z_{\text{eff}}$ ) cause the radius of an anion to be larger than that of the parent atom ([link](#)). For example, a sulfur atom ([Ne]3s<sup>2</sup>3p<sup>4</sup>) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ([Ne]3s<sup>2</sup>3p<sup>6</sup>) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N<sup>3-</sup>, O<sup>2-</sup>, F<sup>-</sup>, Ne, Na<sup>+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup> (1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>). Another isoelectronic series is P<sup>3-</sup>, S<sup>2-</sup>, Cl<sup>-</sup>, Ar, K<sup>+</sup>, Ca<sup>2+</sup>, and Sc<sup>3+</sup> ([Ne]3s<sup>2</sup>3p<sup>6</sup>). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

## Variation in Ionization Energies

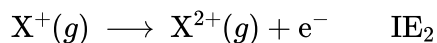
The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE<sub>1</sub>). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

**Equation:**



The energy required to remove the second most loosely bound electron is called the second ionization energy (IE<sub>2</sub>).

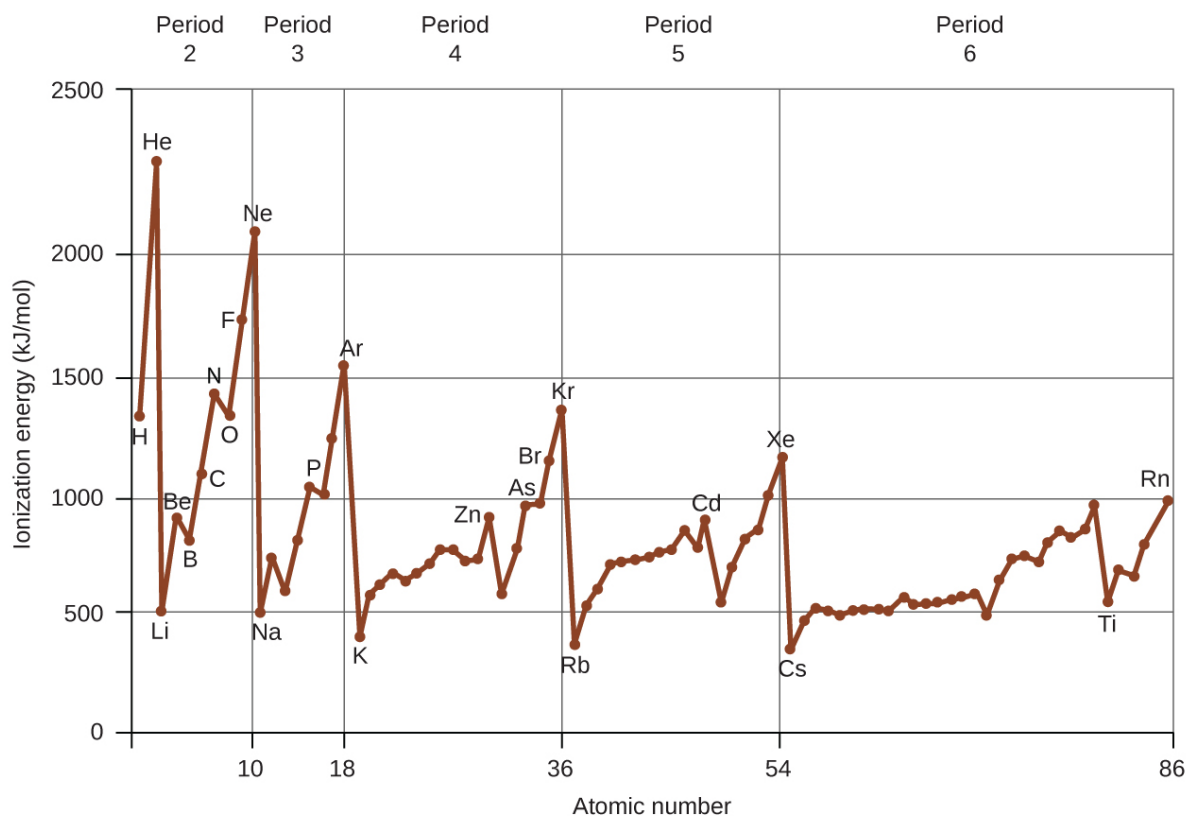
**Equation:**



The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization

energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

[\[link\]](#) graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in [\[link\]](#). Within a period, the  $IE_1$  generally increases with increasing  $Z$ . Down a group, the  $IE_1$  value generally decreases with increasing  $Z$ . There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as  $l$  increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the  $s$  electrons are lower in energy than the  $p$  electrons. This means that an  $s$  electron is harder to remove from an atom than a  $p$  electron in the same shell. The electron removed during the ionization of beryllium ( $[\text{He}]2s^2$ ) is an  $s$  electron, whereas the electron removed during the ionization of boron ( $[\text{He}]2s^22p^1$ ) is a  $p$  electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

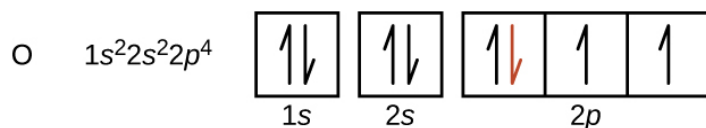


The first ionization energy of the elements in the first five periods are plotted against their atomic number.

		First Ionization Energies of Some Elements (kJ/mol)																	
Period	Group																		
	1											13	14	15	16	17	18		
1	H 1310																	He 2370	
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080	
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520	
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350	
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170	
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At ...	Rn 1030	
7	Fr ...	Ra 510																	

This version of the periodic table shows the first ionization energy ( $IE_1$ ), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing  $IE_1$  values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the  $2p$  orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in [\[link\]](#)).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in [\[link\]](#), there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

#### Successive Ionization Energies for Selected Elements (kJ/mol)

Successive Ionization Energies for Selected Elements (kJ/mol)	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
K	418.8	3051.8	4419.6	5876.9	7075.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

### Example:

#### Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE<sub>1</sub> for Al, IE<sub>1</sub> for Tl, IE<sub>2</sub> for Na, IE<sub>3</sub> for Al.

#### Solution

Removing the  $6p^1$  electron from Tl is easier than removing the  $3p^1$  electron from Al because the higher  $n$  orbital is farther from the nucleus, so  $IE_1(\text{Tl}) < IE_1(\text{Al})$ . Ionizing the third electron from Al ( $\text{Al}^{2+} \rightarrow \text{Al}^{3+} + e^-$ ) requires more energy because the cation  $\text{Al}^{2+}$  exerts a stronger pull on the electron than the neutral Al atom, so  $IE_1(\text{Al}) < IE_3(\text{Al})$ . The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:  $IE_1(\text{Tl}) < IE_1(\text{Al}) < IE_3(\text{Al}) < IE_2(\text{Na})$ .

#### Check Your Learning

Which has the lowest value for IE<sub>1</sub>: O, Po, Pb, or Ba?

#### Note:

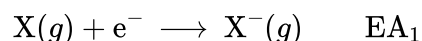
#### Answer:

Ba

## Variation in Electron Affinities

The **electron affinity** (EA) is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

#### Equation:



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in [\[link\]](#). You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a  $-2$  ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher  $n$  level, which is more difficult to do. Group 2 (2A) has a filled  $ns$  subshell, and so the next electron added goes into the higher energy  $np$ , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled  $np$  subshell and the next electron must be paired with an existing  $np$  electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the most negative EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the *second* element in the group most often has the most negative EA. This can be attributed to the small size of the  $n = 2$  shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of  $-348$  kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is  $-322$  kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion ( $F^-$ ), we add an electron to the  $n = 2$  shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the  $n = 3$  shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily, resulting in a more negative EA.

Period		Electron Affinity Values for Selected Elements (kJ/mol)																Group	
		1	2											13	14	15	16	17	18
1		H -72																	He +20*
2		Li -60	Be +240*											B -23	C -123	N 0	O -141	F -322	Ne -30
3		Na -53	Mg +230*											Al -44	Si -120	P -74	S -200	Cl -348	Ar +35*
4		K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*
5		Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*
6		Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*
7		Fr	Ra																

\* Calculated value

This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

## Key Concepts and Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the  $n$  level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

## Chemistry End of Chapter Exercises



**Exercise:**

**Problem:**

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

---

**Solution:**

Cl

**Exercise:**

**Problem:**

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

**Exercise:**

**Problem:**

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

---

**Solution:**

O

**Exercise:**

**Problem:**

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

**Exercise:**

**Problem:**

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

---

**Solution:**

Rb < Li < N < F

**Exercise:**

**Problem:**

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: Mg, O, S, Si

**Exercise:**

**Problem:**

Atoms of which group in the periodic table have a valence shell electron configuration of  $ns^2np^3$ ?

---

**Solution:**

15 (5A)

**Exercise:****Problem:**

Atoms of which group in the periodic table have a valence shell electron configuration of  $ns^2$ ?

**Exercise:****Problem:**

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

---

**Solution:**

$\text{Mg} < \text{Ca} < \text{Rb} < \text{Cs}$

**Exercise:****Problem:**

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

**Exercise:****Problem:**

Based on their positions in the periodic table, list the following ions in order of increasing radius:  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ .

---

**Solution:**

$\text{Si}^{4+} < \text{Al}^{3+} < \text{Ca}^{2+} < \text{K}^+$

**Exercise:**

**Problem:** List the following ions in order of increasing radius:  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Br}^-$ ,  $\text{Te}^{2-}$ .

**Exercise:**

**Problem:** Which atom and/or ion is (are) isoelectronic with  $\text{Br}^+$ :  $\text{Se}^{2+}$ , Se,  $\text{As}^-$ , Kr,  $\text{Ga}^{3+}$ ,  $\text{Cl}^-$ ?

---

**Solution:**

Se,  $\text{As}^-$

**Exercise:**

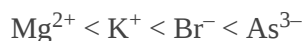
**Problem:**

Which of the following atoms and ions is (are) isoelectronic with  $S^{2+}$ :  $Si^{4+}$ ,  $Cl^{3+}$ , Ar,  $As^{3+}$ , Si,  $Al^{3+}$ ?

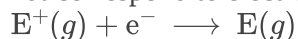
**Exercise:****Problem:**

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius:  $As^{3-}$ ,  $Br^{-}$ ,  $K^{+}$ ,  $Mg^{2+}$ .

---

**Solution:****Exercise:****Problem:**

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: Note the process depicted does *not* correspond to electron affinity.)

**Exercise:****Problem:**

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

**Solution:**

O,  $IE_1$

**Exercise:****Problem:**

The ionic radii of the ions  $S^{2-}$ ,  $Cl^{-}$ , and  $K^{+}$  are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

**Exercise:****Problem:**

Which main group atom would be expected to have the lowest second ionization energy?

---

**Solution:**

Ra

**Exercise:**

**Problem:** Explain why Al is a member of group 13 rather than group 3?

## Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy change associated with addition of an electron to a gaseous atom or ion

ionization energy

energy required to remove an electron from a gaseous atom or ion

isoelectronic

group of ions or atoms that have identical electron configurations

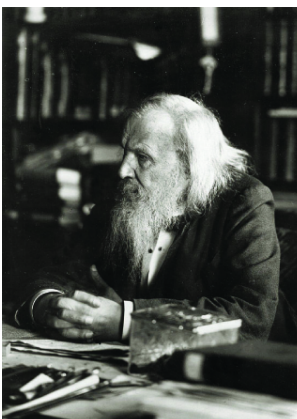
## The Periodic Table

By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized ([link](#)).



(a)

Rechn	Gruppo I. — R <sup>0</sup>	Gruppo II. — R <sup>0</sup>	Gruppo III. — R <sup>0</sup> <sup>a</sup>	Gruppo IV. RH <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppo V. RH <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppo VI. RH <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppo VII. RH <sup>a</sup> R <sup>0</sup> <sup>a</sup>	Gruppo VIII. — R <sup>0</sup> <sup>a</sup>
1	II=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	So=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

(a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column ([link](#)). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.



moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; [\[footnote\]](#) and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; [\[link\]](#)). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group's elements are provided in a chapter on transition metals and coordination chemistry.



Periodic Table of the Elements																		
Group 1		Main group elements																18
2													13	14	15	16	17	
Alkali metals	Alkaline earth metals	3	4	5	6	7	8	9	10	11	12							
		Transition metals																
		Lanthanides																
		Actinides																

The periodic table organizes elements with similar properties into groups.

**Note:**

Click on this [link](#) for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this [one](#) that shows photos of all the elements.

**Example:**

**Naming Groups of Elements**

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

- (a) chlorine
- (b) calcium

(c) sodium

(d) sulfur

**Solution**

The family names are as follows:

(a) halogen

(b) alkaline earth metal

(c) alkali metal

(d) chalcogen

**Check Your Learning**

Give the group name for each of the following elements:

(a) krypton

(b) selenium

(c) barium

(d) lithium

**Note:**

**Answer:**

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

## Key Concepts and Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

- (a) uranium
- (b) bromine
- (c) strontium
- (d) neon
- (e) gold
- (f) americium
- (g) rhodium

(h) sulfur

(i) carbon

(j) potassium

---

**Solution:**

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

**Exercise:**

**Problem:**

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) cobalt

(b) europium

(c) iodine

(d) indium

(e) lithium

(f) oxygen

(g) cadmium

(h) terbium

(i) rhenium

**Exercise:****Problem:**

Using the periodic table, identify the lightest member of each of the following groups:

- (a) noble gases
  - (b) alkaline earth metals
  - (c) alkali metals
  - (d) chalcogens
- 

**Solution:**

- (a) He; (b) Be; (c) Li; (d) O

**Exercise:****Problem:**

Using the periodic table, identify the heaviest member of each of the following groups:

- (a) alkali metals
- (b) chalcogens
- (c) noble gases
- (d) alkaline earth metals

**Exercise:****Problem:**

Use the periodic table to give the name and symbol for each of the following elements:

- (a) the noble gas in the same period as germanium

- (b) the alkaline earth metal in the same period as selenium
  - (c) the halogen in the same period as lithium
  - (d) the chalcogen in the same period as cadmium
- 

**Solution:**

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

**Exercise:**

**Problem:**

Use the periodic table to give the name and symbol for each of the following elements:

- (a) the halogen in the same period as the alkali metal with 11 protons
- (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
- (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
- (d) the noble gas in the same period as gold

**Exercise:**

**Problem:**

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the alkali metal with 11 protons and a mass number of 23
- (b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom
- (c) the isotope with 33 protons and 40 neutrons in its nucleus

(d) the alkaline earth metal with 88 electrons and 138 neutrons

---

**Solution:**

(a)  ${}_{11}^{23}\text{Na}$ ; (b)  ${}_{54}^{129}\text{Xe}$ ; (c)  ${}_{33}^{73}\text{As}$ ; (d)  ${}_{88}^{226}\text{Ra}$

**Exercise:**

**Problem:**

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the chalcogen with a mass number of 125

(b) the halogen whose longest-lived isotope is radioactive

(c) the noble gas, used in lighting, with 10 electrons and 10 neutrons

(d) the lightest alkali metal with three neutrons

**Glossary**

actinide

inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal

element in group 1

alkaline earth metal

element in group 2

chalcogen

element in group 16

group

vertical column of the periodic table

halogen  
element in group 17

inert gas  
(also, noble gas) element in group 18

inner transition metal  
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide  
inner transition metal in the top of the bottom two rows of the periodic table

main-group element  
(also, representative element) element in groups 1, 2, and 13–18

metal  
element that is shiny, malleable, good conductor of heat and electricity

metalloid  
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas  
(also, inert gas) element in group 18

nonmetal  
element that appears dull, poor conductor of heat and electricity

period  
(also, series) horizontal row of the periodic table

periodic law  
properties of the elements are periodic function of their atomic numbers

periodic table



table of the elements that places elements with similar chemical properties close together

pnictogen

element in group 15

representative element

(also, main-group element) element in columns 1, 2, and 12–18

series

(also, period) horizontal row of the period table

transition metal

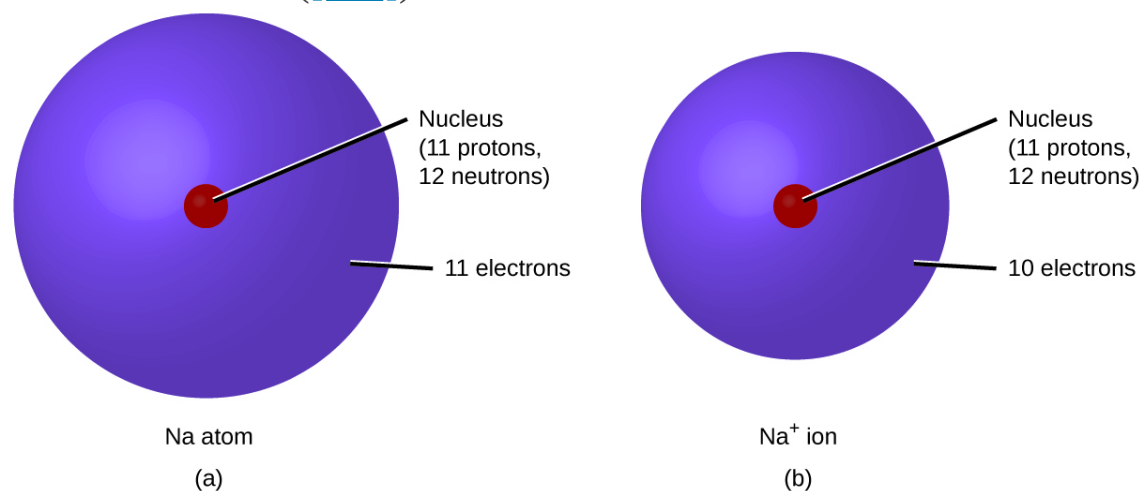
element in groups 3–12 (more strictly defined, 3–11; see chapter on transition metals and coordination chemistry)

## Molecular and Ionic Compounds

By the end of this section, you will be able to:

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions ([\[link\]](#)).



(a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation ( $\text{Na}^+$ ) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas.

To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized  $\text{Ca}^{2+}$ . The name of a metal ion is the same as the name of the metal atom from which it forms, so  $\text{Ca}^{2+}$  is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1- charge; atoms of group 16 gain two electrons and form ions with a 2- charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1- charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized  $\text{Br}^-$ . (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge ([\[link\]](#)). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1- ions; group 16 elements (two groups left) form 2- ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

**Periodic Table of the Elements**

Period	Group 1	Group 2												Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1																			He
2	Li <sup>+</sup>	Be <sup>2+</sup>													C <sup>4-</sup>	N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	Ne
3	Na <sup>+</sup>	Mg <sup>2+</sup>												Al <sup>3+</sup>		P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>	Ar
4	K <sup>+</sup>	Ca <sup>2+</sup>				Cr <sup>3+</sup> Cr <sup>6+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup> Fe <sup>3+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>+</sup> Cu <sup>2+</sup>	Zn <sup>2+</sup>				As <sup>3-</sup>	Se <sup>2-</sup>	Br <sup>-</sup>	Kr
5	Rb <sup>+</sup>	Sr <sup>2+</sup>										Ag <sup>+</sup>	Cd <sup>2+</sup>				Te <sup>2-</sup>	I <sup>-</sup>	Xe
6	Cs <sup>+</sup>	Ba <sup>2+</sup>									Pt <sup>2+</sup>	Au <sup>+</sup> Au <sup>3+</sup>	Hg <sub>2</sub> <sup>2+</sup> Hg <sup>2+</sup>					At <sup>-</sup>	Rn
7	Fr <sup>+</sup>	Ra <sup>2+</sup>																	

*Note: A red box highlights the element in Period 6, Group 2 (Ba<sup>2+</sup>). An arrow points from this box to a separate section of the table below, which shows a regular pattern of ionic charges for elements in Groups 13 through 18.*

Some elements exhibit a regular pattern of ionic charge when they form ions.

### Example:

#### Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

#### Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al<sup>3+</sup>.

#### Check Your Learning

Give the symbol and name for the ion with 34 protons and 36 electrons.

**Note:**

**Answer:**

$\text{Se}^{2-}$ , the selenide ion

**Example:**

**Formation of Ions**

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

**Solution**

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of  $2+$ . The symbol for the ion is  $\text{Mg}^{2+}$ , and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of  $3-$ . The symbol for the ion is  $\text{N}^{3-}$ , and it is called a nitride ion.

**Check Your Learning**

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

**Note:**

**Answer:**

Al will form a cation with a charge of  $3+$ :  $\text{Al}^{3+}$ , an aluminum ion. Carbon will form an anion with a charge of  $4-$ :  $\text{C}^{4-}$ , a carbide ion.

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in [\[link\]](#). **Oxyanions** are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Common Polyatomic Ions			
Name	Formula	Related Acid	Formula
ammonium	$\text{NH}_4^+$		
hydronium	$\text{H}_3\text{O}^+$		
peroxide	$\text{O}_2^{2-}$		
hydroxide	$\text{OH}^-$		
acetate	$\text{CH}_3\text{COO}^-$	acetic acid	$\text{CH}_3\text{COOH}$
cyanide	$\text{CN}^-$	hydrocyanic acid	$\text{HCN}$

Common Polyatomic Ions			
Name	Formula	Related Acid	Formula
azide	$\text{N}_3^-$	hydrazoic acid	$\text{HN}_3$
carbonate	$\text{CO}_3^{2-}$	carbonic acid	$\text{H}_2\text{CO}_3$
bicarbonate	$\text{HCO}_3^-$		
nitrate	$\text{NO}_3^-$	nitric acid	$\text{HNO}_3$
nitrite	$\text{NO}_2^-$	nitrous acid	$\text{HNO}_2$
sulfate	$\text{SO}_4^{2-}$	sulfuric acid	$\text{H}_2\text{SO}_4$
hydrogen sulfate	$\text{HSO}_4^-$		
sulfite	$\text{SO}_3^{2-}$	sulfurous acid	$\text{H}_2\text{SO}_3$
hydrogen sulfite	$\text{HSO}_3^-$		
phosphate	$\text{PO}_4^{3-}$	phosphoric acid	$\text{H}_3\text{PO}_4$
hydrogen phosphate	$\text{HPO}_4^{2-}$		
dihydrogen phosphate	$\text{H}_2\text{PO}_4^-$		
perchlorate	$\text{ClO}_4^-$	perchloric acid	$\text{HClO}_4$

Common Polyatomic Ions			
Name	Formula	Related Acid	Formula
chlorate	$\text{ClO}_3^-$	chloric acid	$\text{HClO}_3$
chlorite	$\text{ClO}_2^-$	chlorous acid	$\text{HClO}_2$
hypochlorite	$\text{ClO}^-$	hypochlorous acid	$\text{HClO}$
chromate	$\text{CrO}_4^{2-}$	chromic acid	$\text{H}_2\text{CrO}_4$
dichromate	$\text{Cr}_2\text{O}_7^{2-}$	dichromic acid	$\text{H}_2\text{Cr}_2\text{O}_7$
permanganate	$\text{MnO}_4^-$	permanganic acid	$\text{HMnO}_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for “hyper”) and *hypo-* (meaning “under”) are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is  $\text{ClO}_4^-$ , chlorate is  $\text{ClO}_3^-$ , chlorite is  $\text{ClO}_2^-$  and hypochlorite is  $\text{ClO}^-$ . Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is  $\text{NO}_3^-$  while sulfate is  $\text{SO}_4^{2-}$ . This will be covered in more detail later in the module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are “shared” and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the



bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

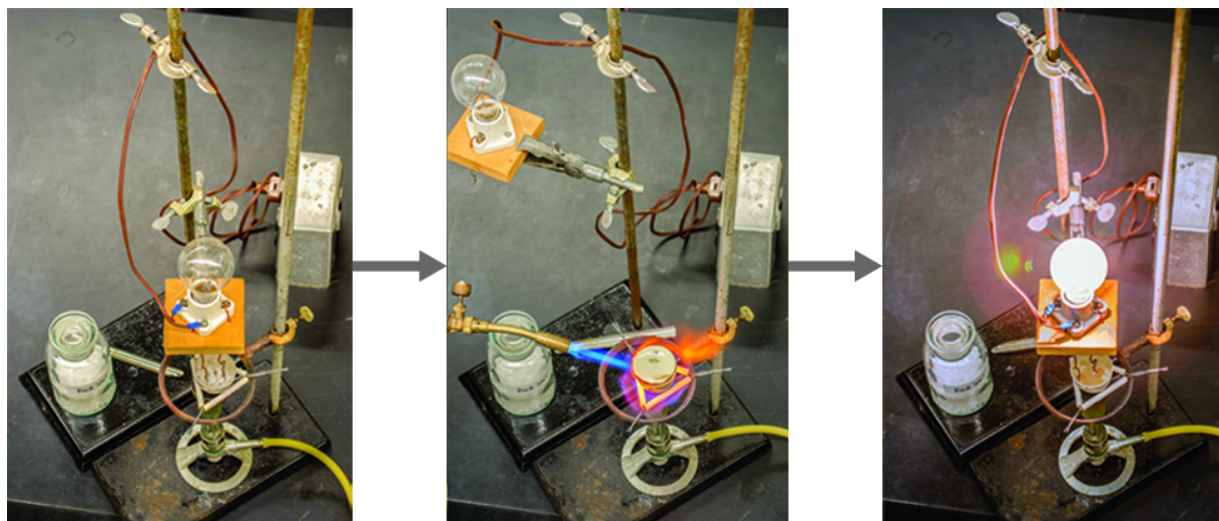
## Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation,  $\text{Na}^+$ , and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion,  $\text{Cl}^-$ , the resulting compound,  $\text{NaCl}$ , is composed of sodium ions and chloride ions in the ratio of one  $\text{Na}^+$  ion for each  $\text{Cl}^-$  ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form  $\text{CaCl}_2$ , which is composed of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions in the ratio of one  $\text{Ca}^{2+}$  ion to two  $\text{Cl}^-$  ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride,  $\text{AlCl}_3$ , is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at  $801\text{ }^\circ\text{C}$  and boils at  $1413\text{ }^\circ\text{C}$ . (As a comparison, the molecular compound water melts at  $0\text{ }^\circ\text{C}$  and boils at  $100\text{ }^\circ\text{C}$ .) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles). When molten, however, it can conduct

electricity because its ions are able to move freely through the liquid ([link](#)).



Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

**Note:**

Watch this [video](#) to see a mixture of salts melt and conduct electricity.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

**Example:****Predicting the Formula of an Ionic Compound**

The gemstone sapphire ([link](#)) is mostly a compound of aluminum and oxygen that contains aluminum cations,  $\text{Al}^{3+}$ , and oxygen anions,  $\text{O}^{2-}$ . What is the formula of this compound?



Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

**Solution**

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of  $3+$ , would give us six positive charges, and three oxide ions, each with a charge of  $2-$ , would give us six negative charges. The formula would be  $\text{Al}_2\text{O}_3$ .

**Check Your Learning**

Predict the formula of the ionic compound formed between the sodium cation,  $\text{Na}^+$ , and the sulfide anion,  $\text{S}^{2-}$ .

**Note:**

**Answer:**



Many ionic compounds contain polyatomic ions ([link](#)) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is  $\text{Ca}_3(\text{PO}_4)_2$ . This formula indicates that there are three calcium ions ( $\text{Ca}^{2+}$ ) for every two phosphate ( $\text{PO}_4^{3-}$ ) groups. The  $\text{PO}_4^{3-}$  groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3-. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

**Example:**

**Predicting the Formula of a Compound with a Polyatomic Anion**

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions  $\text{Ca}^{2+}$  and  $\text{H}_2\text{PO}_4^-$ . What is the formula of this compound?

**Solution**

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one  $\text{Ca}^{2+}$  ion to two  $\text{H}_2\text{PO}_4^-$  ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

**Check Your Learning**

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion,  $\text{O}_2^{2-}$  (Hint: Use the periodic table to predict the sign

and the charge on the lithium ion.)

**Note:**

**Answer:**

$\text{Li}_2\text{O}_2$

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as  $\text{NaCl}$ ) and for many compounds containing polyatomic ions (such as  $\text{CaSO}_4$ ), these formulas are just the empirical formulas introduced earlier. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of  $\text{Na}^+$  and  $\text{C}_2\text{O}_4^{2-}$  ions combined in a 2:1 ratio, and its formula is written as  $\text{Na}_2\text{C}_2\text{O}_4$ . The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula,  $\text{NaCO}_2$ . This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion,  $\text{C}_2\text{O}_4^{2-}$ .

## Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as

gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

**Example:****Predicting the Type of Bonding in Compounds**

Predict whether the following compounds are ionic or molecular:

- (a) KI, the compound used as a source of iodine in table salt
- (b)  $\text{H}_2\text{O}_2$ , the bleach and disinfectant hydrogen peroxide
- (c)  $\text{CHCl}_3$ , the anesthetic chloroform
- (d)  $\text{Li}_2\text{CO}_3$ , a source of lithium in antidepressants

**Solution**

- (a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
- (b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal;  $\text{H}_2\text{O}_2$  is predicted to be molecular.
- (c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal;  $\text{CHCl}_3$  is predicted to be molecular.
- (d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion;  $\text{Li}_2\text{CO}_3$  is predicted to be ionic.

**Check Your Learning**

Using the periodic table, predict whether the following compounds are ionic or covalent:

- (a)  $\text{SO}_2$
- (b)  $\text{CaF}_2$
- (c)  $\text{N}_2\text{H}_4$

(d)  $\text{Al}_2(\text{SO}_4)_3$

**Note:**

**Answer:**

(a) molecular; (b) ionic; (c) molecular; (d) ionic

## Key Concepts and Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:**

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl<sub>3</sub>, ICl, MgCl<sub>2</sub>, PCl<sub>5</sub>, and CCl<sub>4</sub>.

---

**Solution:**

Ionic: KCl, MgCl<sub>2</sub>; Covalent: NCl<sub>3</sub>, ICl, PCl<sub>5</sub>, CCl<sub>4</sub>

**Exercise:****Problem:**

Using the periodic table, predict whether the following chlorides are ionic or covalent: SiCl<sub>4</sub>, PCl<sub>3</sub>, CaCl<sub>2</sub>, CsCl, CuCl<sub>2</sub>, and CrCl<sub>3</sub>.

**Exercise:****Problem:**

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

(a) NF<sub>3</sub>

(b) BaO,

(c) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>

(d) Sr(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>

(e) IBr

(f) Na<sub>2</sub>O

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**Solution:**

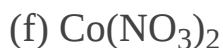
(a) covalent; (b) ionic, Ba<sup>2+</sup>, O<sup>2-</sup>; (c) ionic, NH<sub>4</sub><sup>+</sup>, CO<sub>3</sub><sup>2-</sup>; (d) ionic, Sr<sup>2+</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; (e) covalent; (f) ionic, Na<sup>+</sup>, O<sup>2-</sup>

**Exercise:**

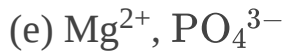
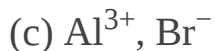
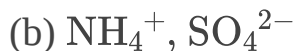
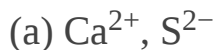


**Problem:**

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

**Exercise:****Problem:**

For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

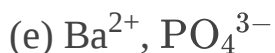
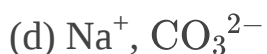
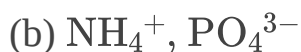


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**Solution:****Exercise:**

**Problem:**

For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

**Glossary**

covalent bond

attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound

(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond

electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound

compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound

(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion

ion composed of a single atom

oxyanion

polyatomic anion composed of a central atom bonded to oxygen atoms

polyatomic ion

ion composed of more than one atom

## Introduction

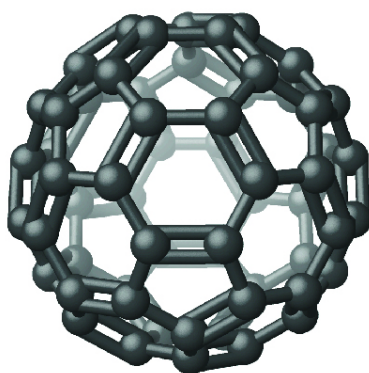
class="introduction"

- Ionic Bonding
- Covalent Bonding
- Lewis Symbols and Structures
- Formal Charges and Resonance
- Strengths of Ionic and Covalent Bonds
- Molecular Structure and Polarity

Nicknamed  
“buckyballs,”  
buckminsterfullerene  
molecules ( $C_{60}$ )  
contain only carbon  
atoms (left) arranged  
to form a geometric  
framework of  
hexagons and  
pentagons, similar to  
the pattern on a  
soccer ball (center).

This molecular  
structure is named  
after architect R.  
Buckminster Fuller,  
whose innovative  
designs combined  
simple geometric  
shapes to create  
large, strong  
structures such as this  
weather radar dome  
near Tucson, Arizona  
(right). (credit  
middle: modification

of work by  
“Petey21”/Wikimedi  
a Commons; credit  
right: modification of  
work by Bill  
Morrow)



It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene. This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula,  $C_{60}$ , and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.

## Ionic Bonding

By the end of this section, you will be able to:

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by **ionic bonds**: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas,  $\text{Cl}_2$ , a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* ([\[link\]](#)). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



(a)



(b)



(c)

(a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

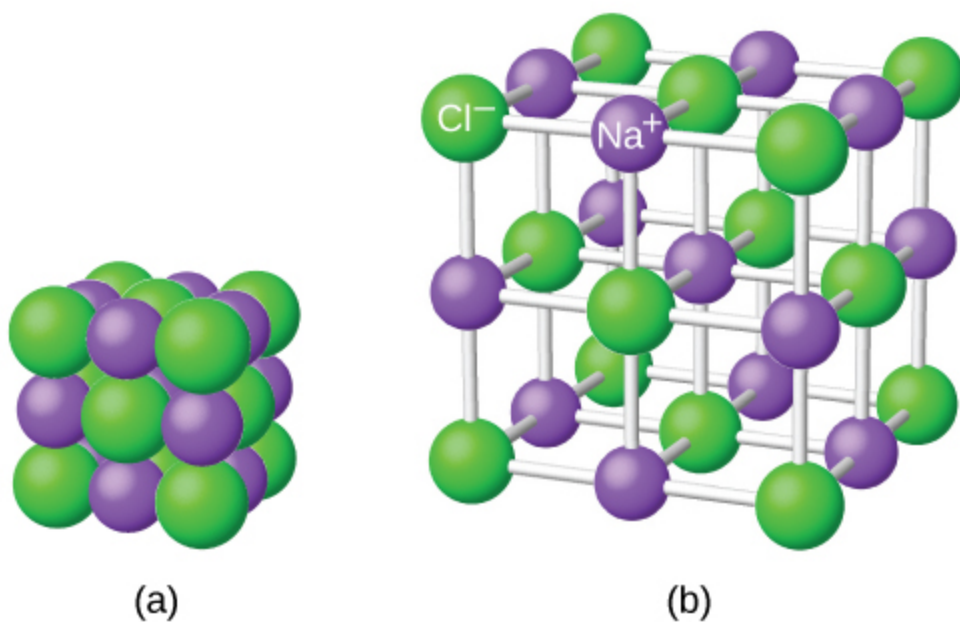
## The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example,  $\text{NaCl}$  is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide,  $\text{Al}_2\text{O}_3$ , indicates that this ionic compound

contains two aluminum cations,  $\text{Al}^{3+}$ , for every three oxide anions,  $\text{O}^{2-}$  [thus,  $(2 \times +3) + (3 \times -2) = 0$ ].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride ( $\text{NaCl}$ ) “molecule” because there is not a single ionic bond, *per se*, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions ([\[link\]](#)).



The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case.



The strong electrostatic attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions:

**Equation:**



## Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ . When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6$ . The  $\text{Ca}^{2+}$  ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions ( $\text{Al}^{3+}$ ).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions  $\text{Tl}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{4+}$ , and  $\text{Bi}^{5+}$ , a partial loss of these atoms' valence shell electrons can also lead to the formation of  $\text{Tl}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the **inert pair effect**, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy

elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion,  $\text{Hg}_2^{2+}$  (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion  $\text{Hg}^{2+}$  (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have  $2+$  or  $3+$  charges that result from the loss of their outermost  $s$  electron(s) first, sometimes followed by the loss of one or two  $d$  electrons from the next-to-outermost shell. For example, iron ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ) forms the ion  $\text{Fe}^{2+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ) by the loss of the  $4s$  electrons and the ion  $\text{Fe}^{3+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ) by the loss of the  $4s$  electron and one of the  $3d$  electrons. Although the  $d$  orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost  $s$  electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a  $3+$  charge, resulting from the loss of their outermost  $s$  electrons and a  $d$  or  $f$  electron.

### **Example:**

#### **Determining the Electronic Structures of Cations**

There are at least 14 elements categorized as “essential trace elements” for the human body. They are called “essential” because they are required for healthy bodily functions, “trace” because they are required only in small amounts, and “elements” in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$ . Write the electron configurations of these cations.

#### **Solution**

First, write the electron configuration for the neutral atoms:

Zn:  $[\text{Ar}]3d^{10}4s^2$

Cr:  $[\text{Ar}]3d^54s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the  $s$  orbital first and then from the  $d$  orbital. For the  $p$ -block elements, electrons are removed from the  $p$  orbitals and then from the  $s$  orbital. Zinc is a member of group 12, so it should have

a charge of  $2+$ , and thus loses only the two electrons in its  $s$  orbital. Chromium is a transition element and should lose its  $s$  electrons and then its  $d$  electrons when forming a cation. Thus, we find the following electron configurations of the ions:



### Check Your Learning

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

#### Note:

#### Answer:



## Electronic Structures of Anions

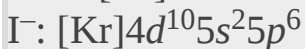
Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer  $s$  and  $p$  orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the  $s$  and  $p$  orbitals of the parent atom. Oxygen, for example, has the electron configuration  $1s^2 2s^2 2p^4$ , whereas the oxygen anion has the electron configuration of the noble gas neon (Ne),  $1s^2 2s^2 2p^6$ . The two additional electrons required to fill the valence orbitals give the oxide ion the charge of  $2-$  ( $\text{O}^{2-}$ ).

#### Example:

#### Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

**Solution**

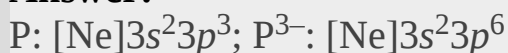


**Check Your Learning**

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

**Note:**

**Answer:**



## Key Concepts and Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:**

Does a cation gain protons to form a positive charge or does it lose electrons?

---

**Solution:**

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

**Exercise:****Problem:**

Iron(III) sulfate  $[\text{Fe}_2(\text{SO}_4)_3]$  is composed of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  ions. Explain why a sample of iron(III) sulfate is uncharged.

**Exercise:****Problem:**

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

---

**Solution:**

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

**Exercise:****Problem:**

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

**Exercise:****Problem:**

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

---

**Solution:**

(a)  $\text{P}^{3-}$ ; (b)  $\text{Mg}^{2+}$ ; (c)  $\text{Al}^{3+}$ ; (d)  $\text{O}^{2-}$ ; (e)  $\text{Cl}^{-}$ ; (f)  $\text{Cs}^{+}$

**Exercise:**

**Problem:**

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

**Exercise:**

**Problem:**

Write the electron configuration for each of the following ions:

(a)  $\text{As}^{3-}$

(b)  $\text{I}^-$

(c)  $\text{Be}^{2+}$

(d)  $\text{Cd}^{2+}$

(e)  $\text{O}^{2-}$

(f)  $\text{Ga}^{3+}$

(g)  $\text{Li}^+$

(h)  $\text{N}^{3-}$

(i)  $\text{Sn}^{2+}$

(j)  $\text{Co}^{2+}$

(k)  $\text{Fe}^{2+}$

(l)  $\text{As}^{3+}$

---

**Solution:**

(a)  $[\text{Ar}]4s^23d^{10}4p^6$ ; (b)  $[\text{Kr}]4d^{10}5s^25p^6$  (c)  $1s^2$  (d)  $[\text{Kr}]4d^{10}$ ; (e)  $[\text{He}]2s^22p^6$ ; (f)  $[\text{Ar}]3d^{10}$ ; (g)  $1s^2$  (h)  $[\text{He}]2s^22p^6$  (i)  $[\text{Kr}]4d^{10}5s^2$  (j)  $[\text{Ar}]3d^7$  (k)  $[\text{Ar}]3d^6$ , (l)  $[\text{Ar}]3d^{10}4s^2$

**Exercise:**

**Problem:**

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

**Exercise:**

**Problem:**

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

(a) Al

(b) Br

(c) Sr

(d) Li

(e) As

(f) S

---

**Solution:**

(a)  $1s^2 2s^2 2p^6 3s^2 3p^1$ ;  $Al^{3+}$ :  $1s^2 2s^2 2p^6$ ; (b)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ; (c)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ ;  $Sr^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ; (d)  $1s^2 2s^1$ ;  $Li^+$ :  $1s^2$ ; (e)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ; (f)  $1s^2 2s^2 2p^6 3s^2 3p^4$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6$



**Exercise:****Problem:**

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

**Glossary**

inert pair effect

tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond

strong electrostatic force of attraction between cations and anions in an ionic compound

## Covalent Bonding

By the end of this section, you will be able to:

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

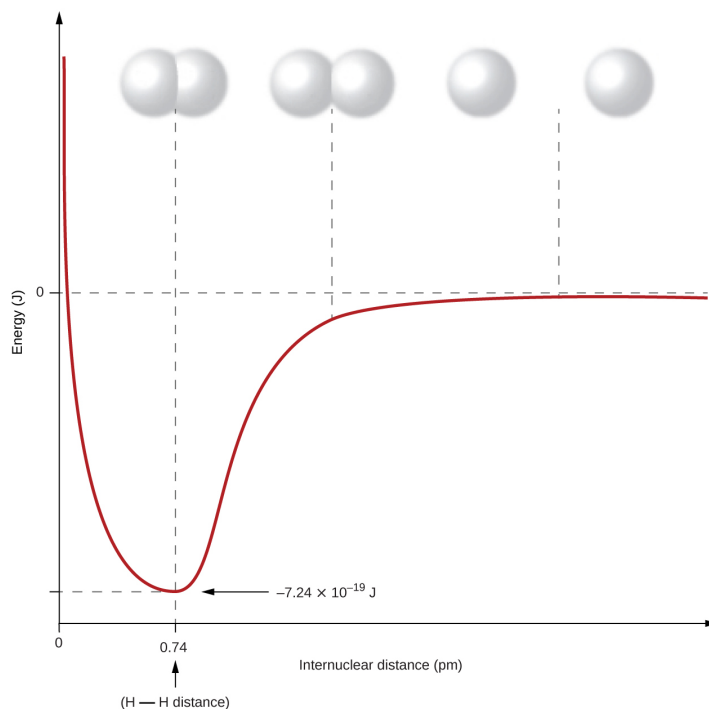
Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a “shared” pair of electrons. Such bonds are called **covalent bonds**. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an  $\text{H}_2$  molecule; each hydrogen atom in the  $\text{H}_2$  molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

## Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule,  $\text{H}_2$ , contains a covalent bond between its two hydrogen atoms. [\[link\]](#) illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the x-axis is the distance between the two atoms. As the two atoms approach each other

(moving left along the  $x$ -axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.

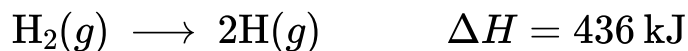


The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases

energy (an exothermic process). In the case of  $\text{H}_2$ , the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

**Equation:**



Conversely, the same amount of energy is released when one mole of  $\text{H}_2$  molecules forms from two moles of H atoms:

**Equation:**

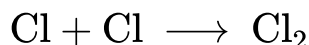


## Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in  $\text{H}_2$ ,  $\text{Cl}_2$ , and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond**. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of  $\text{Cl}_2$ , each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

**Equation:**

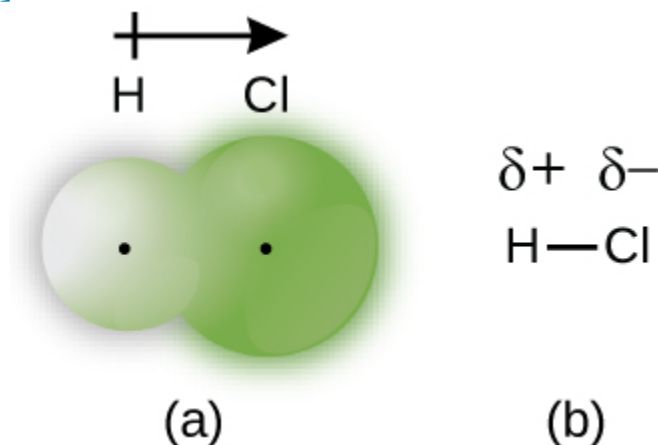


The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical,  $\text{Cl}_2$  also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of

electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. [\[link\]](#) shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to [\[link\]](#), which shows the even distribution of electrons in the H<sub>2</sub> nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,”  $\delta$ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge ( $\delta^+$ ) or a partial negative charge ( $\delta^-$ ). This symbolism is shown for the H–Cl molecule in [\[link\]](#).



(a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols  $\delta^+$  and  $\delta^-$  indicate the polarity of the H–Cl bond.

## Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

[\[link\]](#) shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling ([\[link\]](#)). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with other atoms since they have a full valence shell. (While noble gas compounds such as  $\text{XeO}_2$  do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

Increasing electronegativity →																	
Decreasing electronegativity ↓																	
	Li 1.0	Be 1.5															
	Na 0.9	Mg 1.2															
	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
	Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
	Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np-No 1.4-1.3										

The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

## Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

**Note:**  
Linus Pauling

Linus Pauling, shown in [\[link\]](#), is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



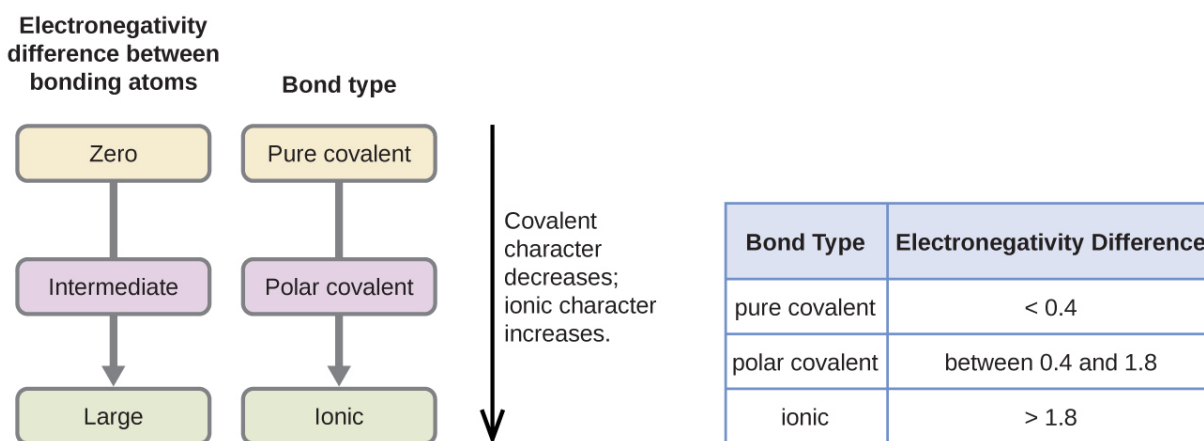
Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.



## Electronegativity and Bond Type

The absolute value of the difference in electronegativity ( $\Delta EN$ ) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). [\[link\]](#) shows the relationship between electronegativity difference and bond type.



As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in [\[link\]](#). This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH<sub>3</sub> a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in

MnI<sub>2</sub> have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, and NH<sub>4</sub><sup>+</sup>, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO<sub>3</sub>, contains the K<sup>+</sup> cation and the polyatomic NO<sub>3</sub><sup>−</sup> anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K<sup>+</sup> and NO<sub>3</sub><sup>−</sup>, as well as covalent between the nitrogen and oxygen atoms in NO<sub>3</sub><sup>−</sup>.

**Example:****Electronegativity and Bond Polarity**

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in [\[link\]](#), arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ<sup>+</sup> and δ<sup>−</sup>:

C–H, C–N, C–O, N–H, O–H, S–H

**Solution**

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ<sup>−</sup> designation is the more electronegative of the two. [\[link\]](#) shows these bonds in order of increasing polarity.

### Bond Polarity and Electronegativity Difference

Bond	$\Delta EN$	Polarity
C–H	0.4	$\delta^- \text{C} - \delta^+ \text{H}$
S–H	0.4	$\delta^- \text{S} - \delta^+ \text{H}$
C–N	0.5	$\delta^+ \text{C} - \delta^- \text{N}$
N–H	0.9	$\delta^- \text{N} - \delta^+ \text{H}$
C–O	1.0	$\delta^+ \text{C} - \delta^- \text{O}$
O–H	1.4	$\delta^- \text{O} - \delta^+ \text{H}$

#### Check Your Learning

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in [\[link\]](#), arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols  $\delta^+$  and  $\delta^-$ .

**Note:**

**Answer:**

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\delta^- \delta^+$ C–H
Si–C	0.7	$\delta^+ \delta^-$ Si–C
Si–O	1.7	$\delta^+ \delta^-$ Si–O

## Key Concepts and Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

## Chemistry End of Chapter Exercises

### Exercise:

**Problem:** Why is it incorrect to speak of a molecule of solid NaCl?

---

**Solution:**

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

**Exercise:**

**Problem:**

What information can you use to predict whether a bond between two atoms is covalent or ionic?

**Exercise:**

**Problem:**

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a)  $\text{Cl}_2\text{CO}$

(b)  $\text{MnO}$

(c)  $\text{NCl}_3$

(d)  $\text{CoBr}_2$

(e)  $\text{K}_2\text{S}$

(f)  $\text{CO}$

(g)  $\text{CaF}_2$

(h)  $\text{HI}$

(i)  $\text{CaO}$

(j) IBr

(k) CO<sub>2</sub>

---

**Solution:**

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

**Exercise:**

**Problem:**

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

**Exercise:**

**Problem:**

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

---

**Solution:**

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

**Exercise:**

**Problem:**

From its position in the periodic table, determine which atom in each pair is more electronegative:

- (a) N or P
- (b) N or Ge
- (c) S or F
- (d) Cl or S
- (e) H or C
- (f) Se or P
- (g) C or Si

**Exercise:****Problem:**

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) C, F, H, N, O
- (b) Br, Cl, F, H, I
- (c) F, H, O, P, S
- (d) Al, H, Na, O, P
- (e) Ba, H, N, O, As

---

**Solution:**

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

**Exercise:****Problem:**

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) As, H, N, P, Sb
- (b) Cl, H, P, S, Si
- (c) Br, Cl, Ge, H, Sr
- (d) Ca, H, K, N, Si
- (e) Cl, Cs, Ge, H, Sr

**Exercise:****Problem:**

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

---

**Solution:**

N, O, F, and Cl

**Exercise:**

**Problem:** Which is the most polar bond?

- (a) C–C
- (b) C–H
- (c) N–H
- (d) O–H
- (e) Se–H



**Exercise:****Problem:**

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

---

**Solution:**

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

**Exercise:****Problem:**

Which of the following molecules or ions contain polar bonds?

(a) O<sub>3</sub>

(b) S<sub>8</sub>

(c) O<sub>2</sub><sup>2-</sup>

(d) NO<sub>3</sub><sup>-</sup>

(e) CO<sub>2</sub>

(f)  $\text{H}_2\text{S}$

(g)  $\text{BH}_4^-$

## Glossary

bond length

distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond

bond formed when electrons are shared between atoms

electronegativity

tendency of an atom to attract electrons in a bond to itself

polar covalent bond

covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond

(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

## Chemical Nomenclature

By the end of this module, you will be able to:

- Derive names for common types of inorganic compounds using a systematic approach

**Nomenclature**, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, CaCO<sub>3</sub>, and N<sub>2</sub>O<sub>4</sub>. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

## Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

## Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *-ide*). Some examples are given in [\[link\]](#).

Names of Some Ionic Compounds	
NaCl, sodium chloride	Na <sub>2</sub> O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI <sub>2</sub> , calcium iodide	Mg <sub>3</sub> N <sub>2</sub> , magnesium nitride
CsF, cesium fluoride	Ca <sub>3</sub> P <sub>2</sub> , calcium phosphide
LiCl, lithium chloride	Al <sub>4</sub> C <sub>3</sub> , aluminum carbide

## Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e., by naming first the cation and then the anion. Examples are shown in [\[link\]](#).

Names of Some Polyatomic Ionic Compounds	
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> , potassium acetate	NH <sub>4</sub> Cl, ammonium chloride
NaHCO <sub>3</sub> , sodium bicarbonate	CaSO <sub>4</sub> , calcium sulfate
Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> , aluminum carbonate	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , magnesium phosphate

### Note:

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in [\[link\]](#). Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

### Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
NaHCO <sub>3</sub> , sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na <sub>2</sub> CO <sub>3</sub> , sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
CaCO <sub>3</sub> calcium carbonate	ingredient in antacids
Mg(OH) <sub>2</sub> , magnesium hydroxide	ingredient in antacids

Everyday Ionic Compounds	
Ionic Compound	Use
$\text{Al}(\text{OH})_3$ , aluminum hydroxide	ingredient in antacids
$\text{NaOH}$ , sodium hydroxide	lye; used as drain cleaner
$\text{K}_3\text{PO}_4$ , potassium phosphate	food additive (many purposes)
$\text{MgSO}_4$ , magnesium sulfate	added to purified water
$\text{Na}_2\text{HPO}_4$ , sodium hydrogen phosphate	anti-caking agent; used in powdered products
$\text{Na}_2\text{SO}_3$ , sodium sulfite	preservative

## Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either  $2+$  or  $3+$  (see [link](#)), and the two corresponding compound formulas are  $\text{FeCl}_2$  and  $\text{FeCl}_3$ . The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II)

chloride and iron(III) chloride, respectively. Other examples are provided in [\[link\]](#).

Some Ionic Compounds with Variably Charged Metal Ions	
Compound	Name
$\text{FeCl}_2$	iron(II) chloride
$\text{FeCl}_3$	iron(III) chloride
$\text{Hg}_2\text{O}$	mercury(I) oxide
$\text{HgO}$	mercury(II) oxide
$\text{SnF}_2$	tin(II) fluoride
$\text{SnF}_4$	tin(IV) fluoride

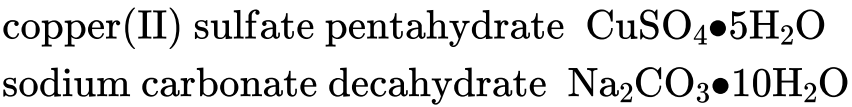
Out-of-date nomenclature used the suffixes *-ic* and *-ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride,  $\text{FeCl}_3$ , was previously called ferric chloride, and iron(II) chloride,  $\text{FeCl}_2$ , was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula  $\text{SnF}_2$ , which is more properly named tin(II) fluoride. The other fluoride of tin is  $\text{SnF}_4$ , which was previously called stannic fluoride but is now named tin(IV) fluoride.

## Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the *anhydrous* (meaning “not hydrated”) compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see [link](#)) and ends with “hydrate.” For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water. The two examples mentioned in the previous paragraph are represented by the formulas

**Equation:**



Nomenclature Prefixes				
Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-



Nomenclature Prefixes				
Number	Prefix		Number	Prefix
4	tetra-		9	nona-
5	penta-		10	deca-

### Example:

#### Naming Ionic Compounds

Name the following ionic compounds:

- (a)  $\text{Fe}_2\text{S}_3$
- (b)  $\text{CuSe}$
- (c)  $\text{GaN}$
- (d)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
- (e)  $\text{Ti}_2(\text{SO}_4)_3$

#### Solution

The anions in these compounds have a fixed negative charge ( $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ,  $\text{N}^{3-}$ , and  $\text{SO}_4^{2-}$ ), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ti}^{3+}$ . These charges are used in the names of the metal ions:

- (a) iron(III) sulfide
- (b) copper(II) selenide
- (c) gallium(III) nitride
- (d) magnesium sulfate heptahydrate
- (e) titanium(III) sulfate

#### Check Your Learning

Write the formulas of the following ionic compounds:

- (a) chromium(III) phosphide
- (b) mercury(II) sulfide
- (c) manganese(II) phosphate
- (d) copper(I) oxide
- (e) iron(III) chloride dihydrate

**Note:**

**Answer:**

(a) CrP; (b) HgS; (c)  $\text{Mn}_3(\text{PO}_4)_2$ ; (d)  $\text{Cu}_2\text{O}$ ; (e)  $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$

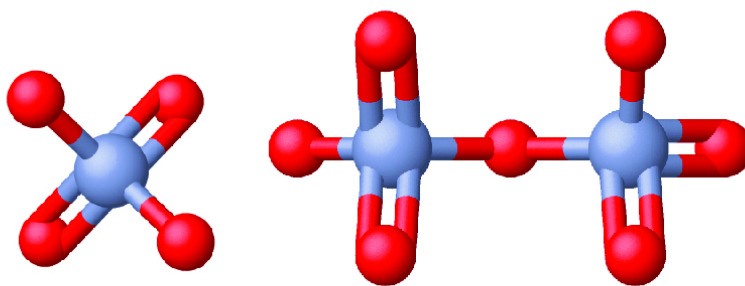
**Note:**

### Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich ([\[link\]](#)) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brockovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—\$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a)



(b)

(a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate,  $\text{CrO}_4^{2-}$  (left), and dichromate,  $\text{Cr}_2\text{O}_7^{2-}$  (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. But Cr(VI) is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

## **Molecular (Covalent) Compounds**

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

### **Compounds Composed of Two Elements**

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO<sub>2</sub>. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method

that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *-ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in [\[link\]](#).

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO<sub>2</sub> is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in [\[link\]](#).

Names of Some Molecular Compounds Composed of Two Elements				
Compound	Name		Compound	Name
SO <sub>2</sub>	sulfur dioxide		BCl <sub>3</sub>	boron trichloride
SO <sub>3</sub>	sulfur trioxide		SF <sub>6</sub>	sulfur hexafluoride
NO <sub>2</sub>	nitrogen dioxide		PF <sub>5</sub>	phosphorus pentafluoride
N <sub>2</sub> O <sub>4</sub>	dinitrogen tetroxide		P <sub>4</sub> O <sub>10</sub>	tetraphosphorus decaoxide
N <sub>2</sub> O <sub>5</sub>	dinitrogen pentoxide		IF <sub>7</sub>	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N<sub>2</sub>O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H<sub>2</sub>O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

**Example:****Naming Covalent Compounds**

Name the following covalent compounds:

- (a) SF<sub>6</sub>
- (b) N<sub>2</sub>O<sub>3</sub>
- (c) Cl<sub>2</sub>O<sub>7</sub>
- (d) P<sub>4</sub>O<sub>6</sub>

**Solution**

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

- (a) sulfur hexafluoride
- (b) dinitrogen trioxide
- (c) dichlorine heptoxide
- (d) tetraphosphorus hexoxide

**Check Your Learning**

Write the formulas for the following compounds:

- (a) phosphorus pentachloride
- (b) dinitrogen monoxide
- (c) iodine heptafluoride
- (d) carbon tetrachloride

**Note:****Answer:**

- (a) PCl<sub>5</sub>; (b) N<sub>2</sub>O; (c) IF<sub>7</sub>; (d) CCl<sub>4</sub>

**Note:**

The following [website](#) provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

## Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions,  $\text{H}^+$ , when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

1. The word “hydrogen” is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word “acid” is added as a second word

For example, when the gas  $\text{HCl}$  (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in [\[link\]](#).

### Names of Some Simple Acids

Name of Gas	Name of Acid
-------------	--------------

Names of Some Simple Acids	
Name of Gas	Name of Acid
HF( <i>g</i> ), hydrogen fluoride	HF( <i>aq</i> ), hydrofluoric acid
HCl( <i>g</i> ), hydrogen chloride	HCl( <i>aq</i> ), hydrochloric acid
HBr( <i>g</i> ), hydrogen bromide	HBr( <i>aq</i> ), hydrobromic acid
HI( <i>g</i> ), hydrogen iodide	HI( <i>aq</i> ), hydroiodic acid
H <sub>2</sub> S( <i>g</i> ), hydrogen sulfide	H <sub>2</sub> S( <i>aq</i> ), hydrosulfuric acid

## Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as **oxyacids**, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit “hydrogen”
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add “acid”

For example, consider H<sub>2</sub>CO<sub>3</sub> (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replaced with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in [\[link\]](#). There are some

exceptions to the general naming method (e.g.,  $\text{H}_2\text{SO}_4$  is called sulfuric acid, not sulfic acid, and  $\text{H}_2\text{SO}_3$  is sulfurous, not sulfous, acid).

Names of Common Oxyacids		
Formula	Anion Name	Acid Name
$\text{HC}_2\text{H}_3\text{O}_2$	acetate	acetic acid
$\text{HNO}_3$	nitrate	nitric acid
$\text{HNO}_2$	nitrite	nitrous acid
$\text{HClO}_4$	perchlorate	perchloric acid
$\text{H}_2\text{CO}_3$	carbonate	carbonic acid
$\text{H}_2\text{SO}_4$	sulfate	sulfuric acid
$\text{H}_2\text{SO}_3$	sulfite	sulfurous acid
$\text{H}_3\text{PO}_4$	phosphate	phosphoric acid

## Key Concepts and Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *-ide*. For example,  $\text{K}_2\text{O}$  is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus,  $\text{FeCl}_2$  is iron(II)



chloride and  $\text{FeCl}_3$  is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include  $\text{SF}_6$ , sulfur hexafluoride, and  $\text{N}_2\text{O}_4$ , dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *-ide* suffix to *-ic*, and adding “acid;”  $\text{HCl}$  is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *-ic* and *-ite* to *-ous*), and adding “acid;”  $\text{H}_2\text{CO}_3$  is carbonic acid.

## Chemistry End of Chapter Exercises

### Exercise:

**Problem:** Name the following compounds:

- (a)  $\text{CsCl}$
- (b)  $\text{BaO}$
- (c)  $\text{K}_2\text{S}$
- (d)  $\text{BeCl}_2$
- (e)  $\text{HBr}$
- (f)  $\text{AlF}_3$

---

### Solution:

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

### Exercise:

**Problem:** Name the following compounds:

- (a) NaF
- (b) Rb<sub>2</sub>O
- (c) BCl<sub>3</sub>
- (d) H<sub>2</sub>Se
- (e) P<sub>4</sub>O<sub>6</sub>
- (f) ICl<sub>3</sub>

**Exercise:**

**Problem:** Write the formulas of the following compounds:

- (a) rubidium bromide
- (b) magnesium selenide
- (c) sodium oxide
- (d) calcium chloride
- (e) hydrogen fluoride
- (f) gallium phosphide
- (g) aluminum bromide
- (h) ammonium sulfate

---

**Solution:**

- (a) RbBr; (b) MgSe; (c) Na<sub>2</sub>O; (d) CaCl<sub>2</sub>; (e) HF; (f) GaP; (g) AlBr<sub>3</sub>;  
(h) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

**Exercise:**

**Problem:** Write the formulas of the following compounds:

- (a) lithium carbonate
- (b) sodium perchlorate
- (c) barium hydroxide
- (d) ammonium carbonate
- (e) sulfuric acid
- (f) calcium acetate
- (g) magnesium phosphate
- (h) sodium sulfite

**Exercise:**

**Problem:** Write the formulas of the following compounds:

- (a) chlorine dioxide
  - (b) dinitrogen tetroxide
  - (c) potassium phosphide
  - (d) silver(I) sulfide
  - (e) aluminum fluoride trihydrate
  - (f) silicon dioxide
- 

**Solution:**

(a)  $\text{ClO}_2$ ; (b)  $\text{N}_2\text{O}_4$ ; (c)  $\text{K}_3\text{P}$ ; (d)  $\text{Ag}_2\text{S}$ ; (e)  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ ; (f)  $\text{SiO}_2$

**Exercise:**

**Problem:** Write the formulas of the following compounds:

- (a) barium chloride
- (b) magnesium nitride
- (c) sulfur dioxide
- (d) nitrogen trichloride
- (e) dinitrogen trioxide
- (f) tin(IV) chloride

**Exercise:**

**Problem:**

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a)  $\text{Cr}_2\text{O}_3$
- (b)  $\text{FeCl}_2$
- (c)  $\text{CrO}_3$
- (d)  $\text{TiCl}_4$
- (e)  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
- (f)  $\text{MoS}_2$

---

**Solution:**

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) chloride hexahydrate; (f) molybdenum(IV) sulfide

**Exercise:**

**Problem:**

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a)  $\text{NiCO}_3$
- (b)  $\text{MoO}_3$
- (c)  $\text{Co}(\text{NO}_3)_2$
- (d)  $\text{V}_2\text{O}_5$
- (e)  $\text{MnO}_2$
- (f)  $\text{Fe}_2\text{O}_3$

**Exercise:****Problem:**

The following ionic compounds are found in common household products. Write the formulas for each compound:

- (a) potassium phosphate
- (b) copper(II) sulfate
- (c) calcium chloride
- (d) titanium(IV) oxide
- (e) ammonium nitrate
- (f) sodium bisulfate (the common name for sodium hydrogen sulfate)

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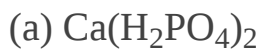
**Solution:**

- (a)  $\text{K}_3\text{PO}_4$ ; (b)  $\text{CuSO}_4$ ; (c)  $\text{CaCl}_2$ ; (d)  $\text{TiO}_2$ ; (e)  $\text{NH}_4\text{NO}_3$ ; (f)  $\text{NaHSO}_4$

**Exercise:**

**Problem:**

The following ionic compounds are found in common household products. Name each of the compounds:

**Exercise:**

**Problem:** What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ )

(c) ferric nitrate [ $\text{Fe}(\text{NO}_3)_3$ ]

(d) titanium tetrachloride

(e) cupric bromide ( $\text{CuBr}_2$ )

---

**Solution:**

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate;  
(d) titanium(IV) chloride; (e) copper(II) bromide

**Glossary**

binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release  $\text{H}^+$  ions when dissolved in water)

binary compound

compound containing two different elements.

nomenclature

system of rules for naming objects of interest

oxyacid

compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release  $\text{H}^+$  ions when dissolved in water)

## Lewis Symbols and Structures

By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

### Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons:



[\[link\]](#) shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	$\text{Na}\cdot$
magnesium	$[\text{Ne}]3s^2$	$\cdot\text{Mg}\cdot$
aluminum	$[\text{Ne}]3s^23p^1$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{Al}}}\cdot$
silicon	$[\text{Ne}]3s^23p^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Si}}}}\cdot$
phosphorus	$[\text{Ne}]3s^23p^3$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}}\cdot$
sulfur	$[\text{Ne}]3s^23p^4$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}}\cdot$
chlorine	$[\text{Ne}]3s^23p^5$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}}}\cdot$
argon	$[\text{Ne}]3s^23p^6$	$:\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}}}}:$

Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.



Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



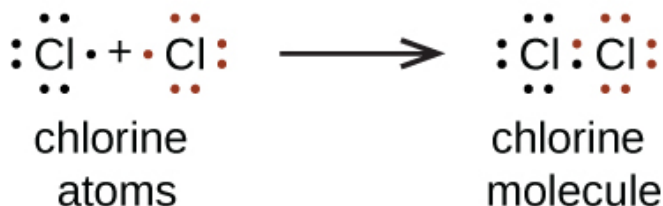
[\[link\]](#) demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$\cdot \ddot{\text{Cl}} \cdot$ chlorine atom	$\longrightarrow$	$\text{Na}^+ \left[ \cdot \ddot{\text{Cl}} \cdot \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot \text{Mg} \cdot$ magnesium atom	+	$\cdot \ddot{\text{O}} \cdot$ oxygen atom	$\longrightarrow$	$\text{Mg}^{2+} \left[ \cdot \ddot{\text{O}} \cdot \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot \text{Ca} \cdot$ calcium atom	+	$2 \cdot \ddot{\text{F}} \cdot$ fluorine atoms	$\longrightarrow$	$\text{Ca}^{2+} \left[ \cdot \ddot{\text{F}} \cdot \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

## Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:



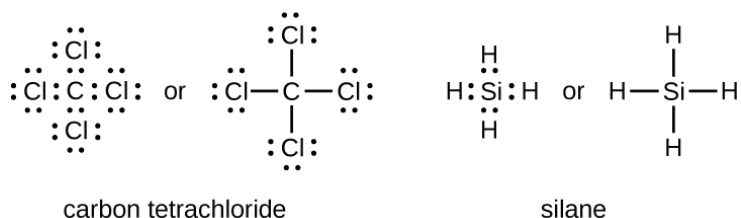
A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

## The Octet Rule

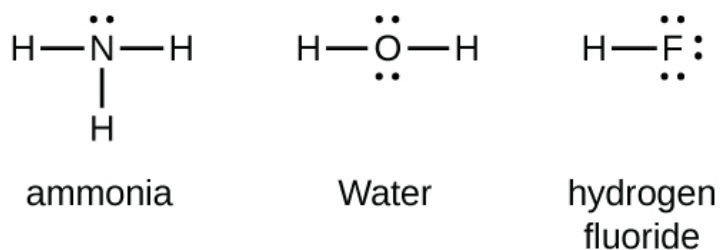
The other halogen molecules ( $\text{F}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , and  $\text{At}_2$ ) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in  $\text{CCl}_4$  (carbon tetrachloride) and silicon in  $\text{SiH}_4$  (silane). Because hydrogen only needs two electrons

to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

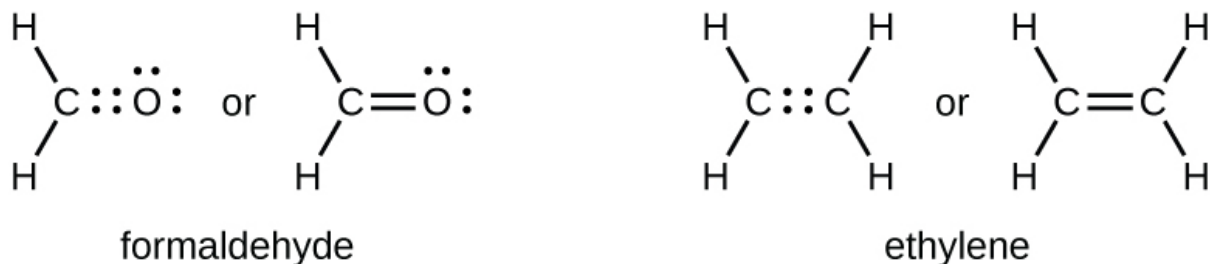


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in  $\text{NH}_3$  (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:

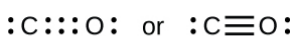


## Double and Triple Bonds

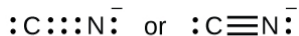
As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in  $\text{CH}_2\text{O}$  (formaldehyde) and between the two carbon atoms in  $\text{C}_2\text{H}_4$  (ethylene):



A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide ( $\text{CO}$ ) and the cyanide ion ( $\text{CN}^-$ ):



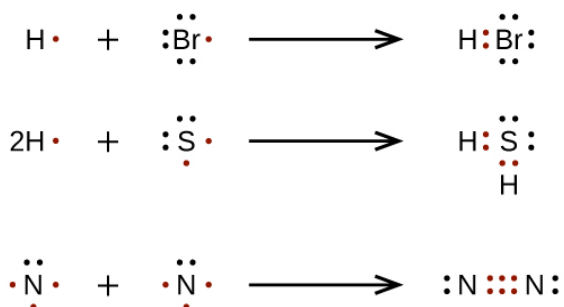
carbon monoxide



cyanide ion

## Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ ,  $\text{NO}^+$ , and  $\text{OF}_2$  as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
  - For a molecule, we add the number of valence electrons on each atom in the molecule:

**Equation:**



$$\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4$$

$$+ \text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4$$

$$= 8 \text{ valence electrons}$$

- For a *negative ion*, such as  $\text{CHO}_2^-$ , we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

**Equation:**



$$\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4$$

$$\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1$$

$$\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12$$

$$+ \quad \quad \quad 1 \text{ additional electron} = 1$$

$$= 18 \text{ valence electrons}$$

- For a *positive ion*, such as  $\text{NO}^+$ , we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

**Equation:**



$$\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5$$

$$\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6$$

$$+ \text{ } -1 \text{ electron (positive charge)} = -1$$

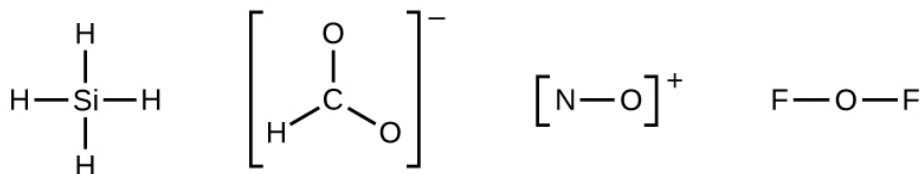
$$= 10 \text{ valence electrons}$$

- Since  $\text{OF}_2$  is a neutral molecule, we simply add the number of valence electrons:

### Equation:

$$\begin{aligned}\text{OF}_2 \\ \text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} &= 6 \\ + \text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} &= 14 \\ &= 20 \text{ valence electrons}\end{aligned}$$

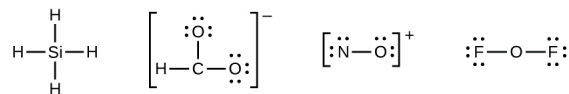
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



When several arrangements of atoms are possible, as for  $\text{CHO}_2^-$ , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In  $\text{CHO}_2^-$ , the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in  $\text{POCl}_3$ , S in  $\text{SO}_2$ , and Cl in  $\text{ClO}_4^-$ . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

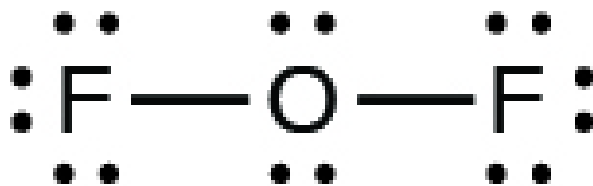
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- There are no remaining electrons on  $\text{SiH}_4$ , so it is unchanged:



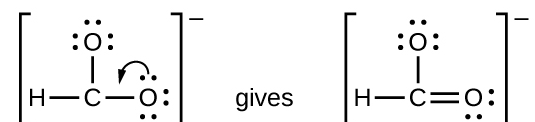
4. Place all remaining electrons on the central atom.

- For  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ , and  $\text{NO}^+$ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For  $\text{OF}_2$ , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

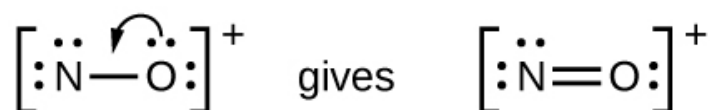


5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

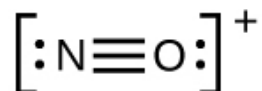
- $\text{SiH}_4$ : Si already has an octet, so nothing needs to be done.
- $\text{CHO}_2^-$ : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- $\text{NO}^+$ : For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In  $\text{OF}_2$ , each atom has an octet as drawn, so nothing changes.

### Example:

#### Writing Lewis Structures

NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane ( $\text{H}_3\text{CCH}_3$ ),

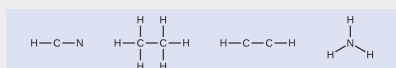
acetylene (HCCH), and ammonia (NH<sub>3</sub>). What are the Lewis structures of these molecules?

### Solution

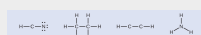
Calculate the number of valence electrons.

HCN: $(1 \times 1) + (1 \times 1) + (5 \times 1) = 7$	H <sub>3</sub> CCH <sub>3</sub> : $(1 \times 3) + (4 \times 2) = 14$	HCCH: $(1 \times 1) + (4 \times 2) = 9$	NH <sub>3</sub> : $(1 \times 1) + (5 \times 1) = 8$
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Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

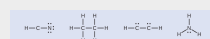


Where needed, distribute electrons to the terminal atoms:



HCN: six electrons placed on N	H <sub>3</sub> CCH <sub>3</sub> : no electrons remain	HCCH: no terminal atoms capable of accepting electrons	NH <sub>3</sub> : no terminal atoms capable of accepting electrons
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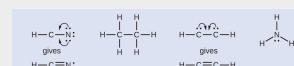
Where needed, place remaining electrons on the central atom:



HCN: no electrons remain	H <sub>3</sub> CCH <sub>3</sub> : no electrons remain	HCCH: four electrons placed on carbon	NH <sub>3</sub> : two electrons placed on nitrogen
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Where needed, rearrange electrons to form two multiple bonds in order to obtain an octet on each atom:

HCN: form two bonds C-N	H <sub>3</sub> CCH <sub>3</sub> : all atoms have the correct number of electrons	HCCH: form a triple bond between the two carbon atoms	NH <sub>3</sub> : all atoms have the correct number of electrons
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### Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO<sub>2</sub> has been implicated in global climate change. What are the Lewis structures of these two molecules?



**Note:**

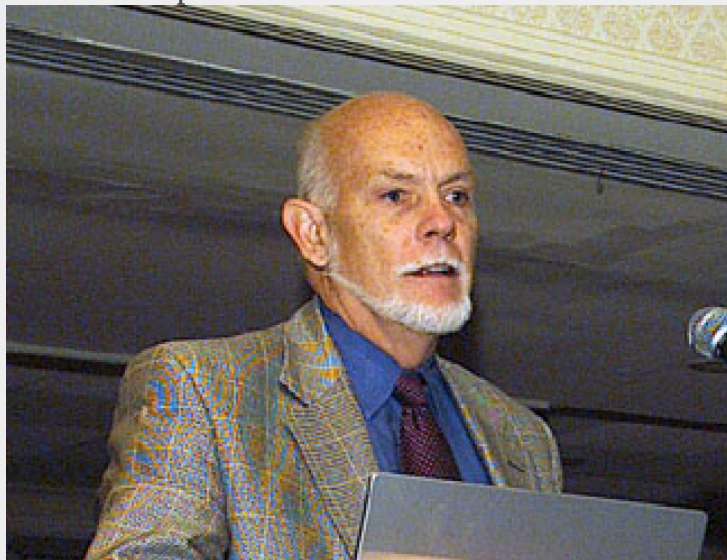
**Answer:**



**Note:**

### Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley ([link](#)), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C<sub>60</sub> buckminsterfullerene molecule ([link](#)). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C<sub>60</sub>. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.



Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates

for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy)

## Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

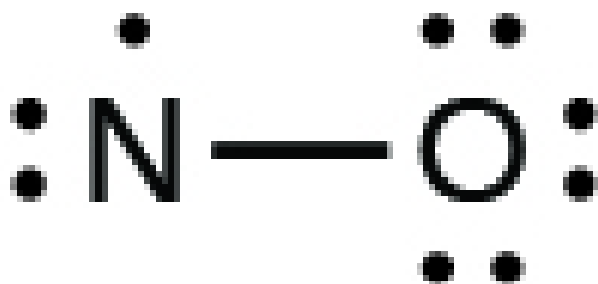
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

### Odd-electron Molecules

We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond:  
N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:



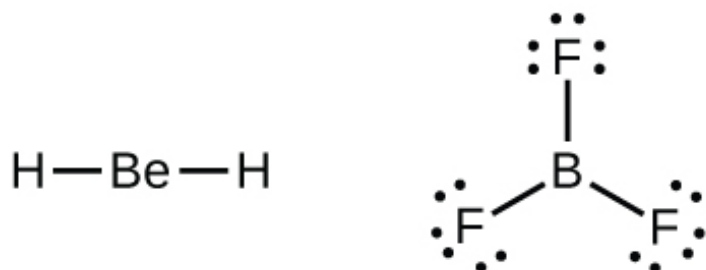
4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)



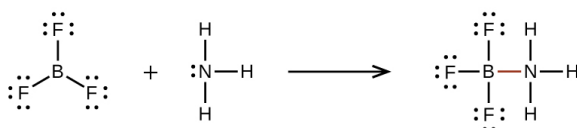
### Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride,  $\text{BeH}_2$ , and boron trifluoride,  $\text{BF}_3$ , the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in  $\text{BF}_3$ , satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient

boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.

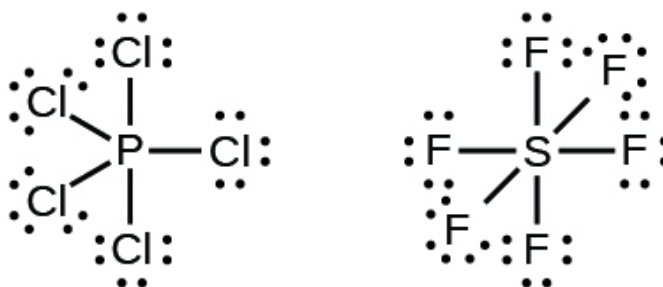


An atom like the boron atom in  $\text{BF}_3$ , which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example,  $\text{NH}_3$  reacts with  $\text{BF}_3$  because the lone pair on nitrogen can be shared with the boron atom:



## Hypervalent Molecules

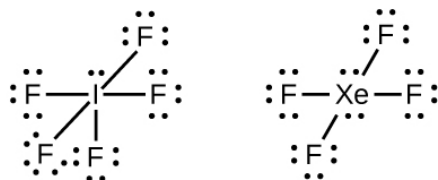
Elements in the second period of the periodic table ( $n = 2$ ) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one  $2s$  and three  $2p$  orbitals). Elements in the third and higher periods ( $n \geq 3$ ) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty  $d$  orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. [\[link\]](#) shows the Lewis structures for two hypervalent molecules,  $\text{PCl}_5$  and  $\text{SF}_6$ .



In  $\text{PCl}_5$ , the central atom phosphorus shares five pairs of electrons. In  $\text{SF}_6$ , sulfur shares six

pairs of electrons.

In some hypervalent molecules, such as  $\text{IF}_5$  and  $\text{XeF}_4$ , some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

### Example:

#### Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined  $\text{XeF}_4$  earlier. What are the Lewis structures of  $\text{XeF}_2$  and  $\text{XeF}_6$ ?

#### Solution

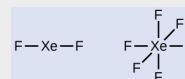
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

*Calculate the number of valence electrons:*

$$\begin{array}{l} \text{XeF}_2: 8 + \quad \times 7 = \\ \quad \quad \quad (2 \quad \quad 22) \end{array} \quad \begin{array}{l} \text{XeF}_6: 8 + \quad \times 7 = \\ \quad \quad \quad (6 \quad \quad 50) \end{array}$$

*Draw a skeleton joining the atoms by single bonds.*

Xenon will be the central atom because fluorine cannot be a central atom:



*Distribute the remaining electrons.*

$\text{XeF}_2$ : We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These

d orbitals and 2s shows two bonding pairs and three lone pairs of electrons can accommodate more than eight electrons. The Lewis structure of  $\text{XeF}_2$

$\text{XeF}_6$ : We place three lone pairs of electrons around each F atom, accounting for 36 electrons.

lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell

around the Xe atom:

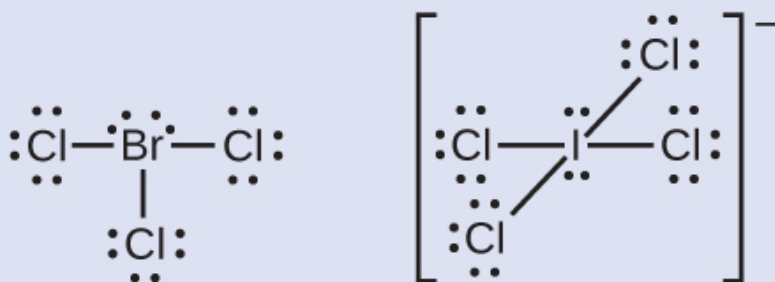
Two electrons remain, and this lone pair is placed on the Xe atom:

### Check Your Learning

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens  $\text{BrCl}_3$  and  $\text{ICl}_4^-$ .

**Note:**

**Answer:**



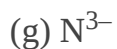
## Key Concepts and Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

## Chemistry End of Chapter Exercises

### Exercise:

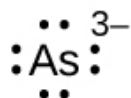
**Problem:** Write the Lewis symbols for each of the following ions:



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### Solution:

(a) eight electrons:

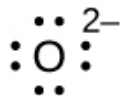


(b) eight electrons:



(c) no electrons  $\text{Be}^{2+}$

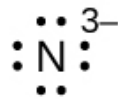
(d) eight electrons:



(e) no electrons  $\text{Ga}^{3+}$

(g) eight electrons:

(g) eight electrons:



### Problem:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

### Problem:

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b)  $\text{Al}_2\text{O}_3$

(c)  $\text{GaCl}_3$

(d)  $\text{K}_2\text{O}$



(e)  $\text{Li}_3\text{N}$

(f)  $\text{KF}$

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**Solution:**

(a)



(b)



(c)



(d)



(e)



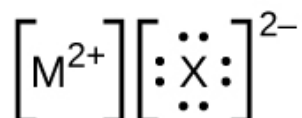
(f)



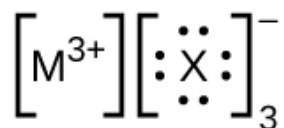
**Exercise:****Problem:**

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

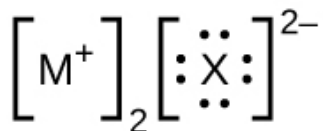
(a)



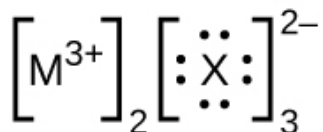
(b)



(c)



(d)

**Exercise:****Problem:**

Write the Lewis structure for the diatomic molecule  $\text{P}_2$ , an unstable form of phosphorus found in high-temperature phosphorus vapor.

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**Solution:**



**Exercise:**

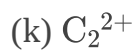
**Problem:** Write Lewis structures for the following:

- (a)  $\text{H}_2$
- (b)  $\text{HBr}$
- (c)  $\text{PCl}_3$
- (d)  $\text{SF}_2$
- (e)  $\text{H}_2\text{CCH}_2$
- (f)  $\text{HNNH}$
- (g)  $\text{H}_2\text{CNH}$
- (h)  $\text{NO}^-$
- (i)  $\text{N}_2$
- (j)  $\text{CO}$
- (k)  $\text{CN}^-$

**Exercise:**

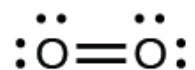
**Problem:** Write Lewis structures for the following:

- (a)  $\text{O}_2$
- (b)  $\text{H}_2\text{CO}$
- (c)  $\text{AsF}_3$
- (d)  $\text{ClNO}$
- (e)  $\text{SiCl}_4$
- (f)  $\text{H}_3\text{O}^+$



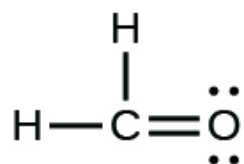
**Solution:**

(a)

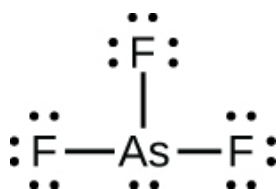


In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

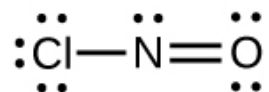
(b)



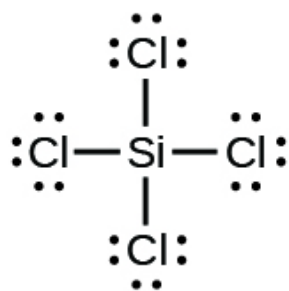
(c)



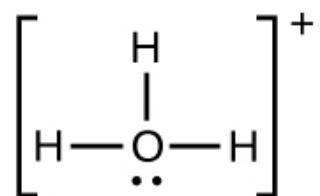
(d)



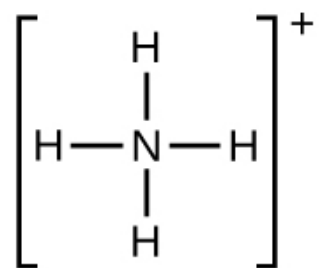
(e)



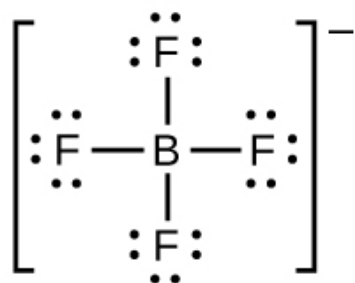
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(g)



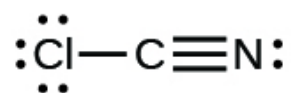
(h)



(i)



(j)



(k)



**Exercise:**

**Problem:** Write Lewis structures for the following:

(a)  $\text{ClF}_3$

(b)  $\text{PCl}_5$

(c)  $\text{BF}_3$

(d)  $\text{PF}_6^-$

**Exercise:**

**Problem:** Write Lewis structures for the following:

(a)  $\text{SeF}_6$

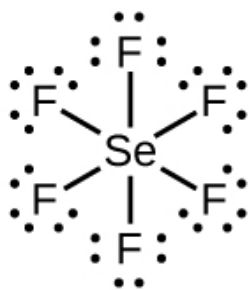
(b)  $\text{XeF}_4$

(c)  $\text{SeCl}_3^+$

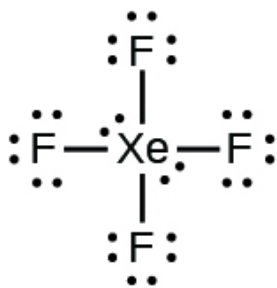
(d)  $\text{Cl}_2\text{BBCl}_2$  (contains a B–B bond)

**Solution:**

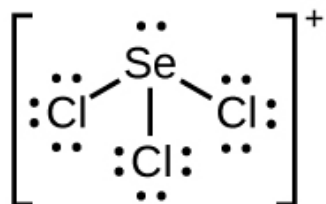
(a)  $\text{SeF}_6$ :



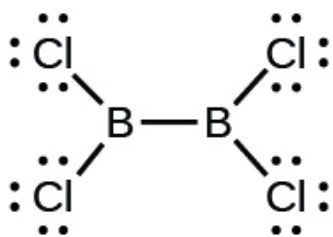
(b) XeF<sub>4</sub>:



(c) SeCl<sub>3</sub><sup>+</sup>:



(d) Cl<sub>2</sub>BBCl<sub>2</sub>:



**Exercise:**

**Problem:** Write Lewis structures for:



**Exercise:**

**Problem:**

Correct the following statement: “The bonds in solid  $\text{PbCl}_2$  are ionic; the bond in a  $\text{HCl}$  molecule is covalent. Thus, all of the valence electrons in  $\text{PbCl}_2$  are located on the  $\text{Cl}^-$  ions, and all of the valence electrons in a  $\text{HCl}$  molecule are shared between the H and Cl atoms.”

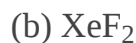
---

**Solution:**

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting  $\text{Pb}^{2+}$  ion has a  $6s^2$  valence shell configuration. Two of the valence electrons in the  $\text{HCl}$  molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

**Exercise:**

**Problem:** Write Lewis structures for the following molecules or ions:



**Exercise:**

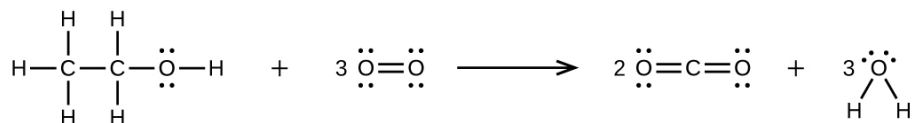
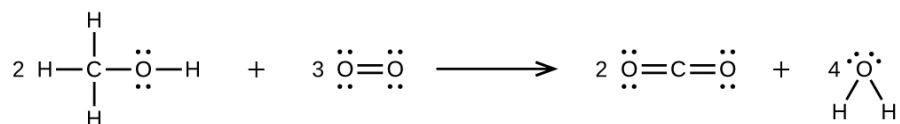
**Problem:**

Methanol,  $\text{H}_3\text{COH}$ , is used as the fuel in some race cars. Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is used extensively as motor fuel in Brazil. Both methanol and ethanol produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

---

**Solution:**





### Exercise:

#### Problem:

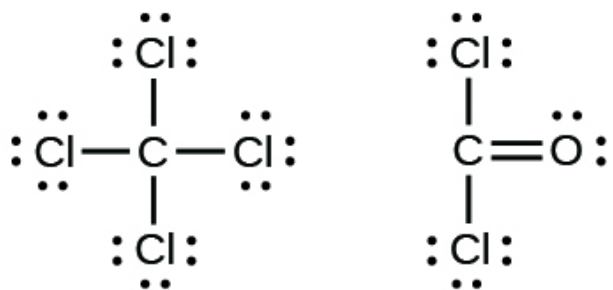
Many planets in our solar system contain organic chemicals including methane ( $\text{CH}_4$ ) and traces of ethylene ( $\text{C}_2\text{H}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propyne ( $\text{H}_3\text{CCCH}$ ), and diacetylene ( $\text{HCCCCCH}$ ). Write the Lewis structures for each of these molecules.

### Exercise:

#### Problem:

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene,  $\text{Cl}_2\text{CO}$ . Write the Lewis structures for carbon tetrachloride and phosgene.

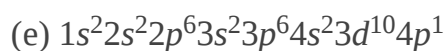
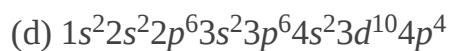
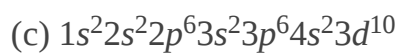
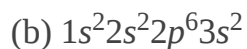
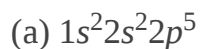
#### Solution:



### Exercise:

#### Problem:

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

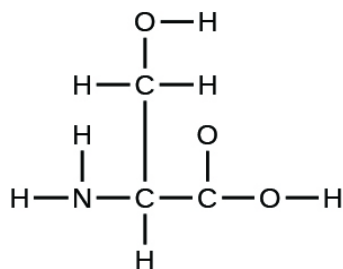


**Exercise:**

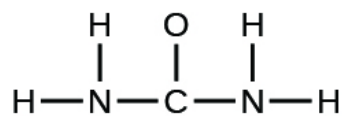
**Problem:**

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

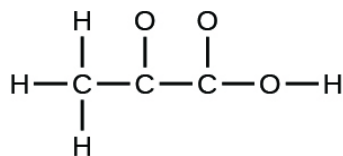
(a) the amino acid serine:



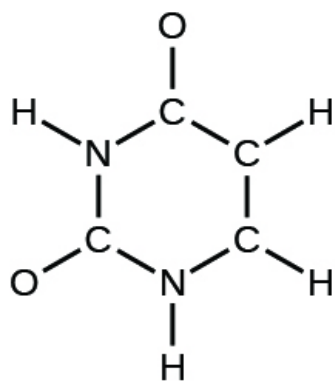
(b) urea:



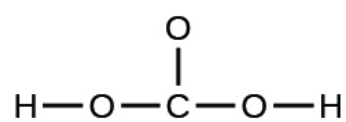
(c) pyruvic acid:



(d) uracil:



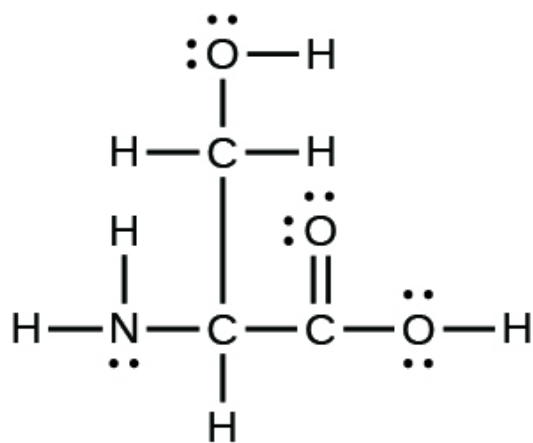
(e) carbonic acid:



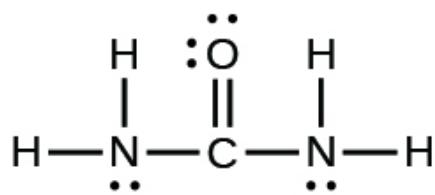

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**Solution:**

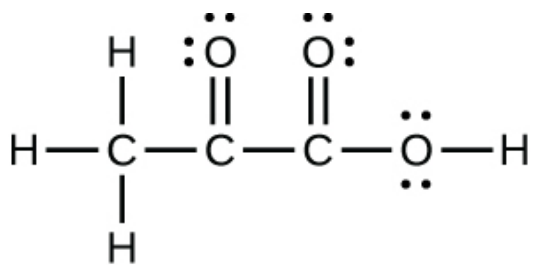
(a)



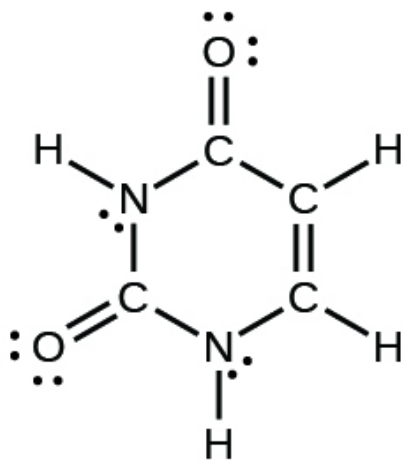
(b)



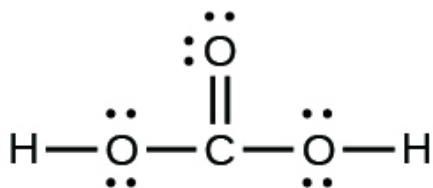
(c)



(d)



(e)



### Exercise:

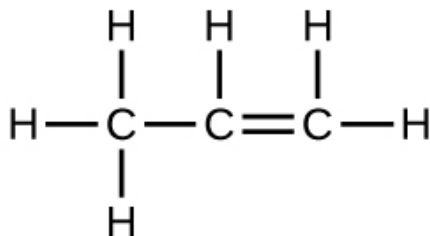
#### Problem:

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

**Exercise:****Problem:**

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

---

**Solution:****Exercise:****Problem:**

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

**Exercise:**

**Problem:** How are single, double, and triple bonds similar? How do they differ?

---

**Solution:**

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

**Glossary**

double bond

covalent bond in which two pairs of electrons are shared between two atoms

free radical

molecule that contains an odd number of electrons

hypervalent molecule

molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure

diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol

symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair

two (a pair of) valence electrons that are not used to form a covalent bond

octet rule

guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond

bond in which a single pair of electrons is shared between two atoms

triple bond

bond in which three pairs of electrons are shared between two atoms

## Formal Charges and Resonance

By the end of this section, you will be able to:

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

## Calculating Formal Charge

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

**Equation:**

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

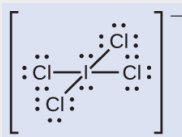
### Example:

#### Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion  $\text{ICl}_4^-$ .

#### Solution

We divide the bonding electron pairs equally for all I–Cl bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:  $\text{I: } 7 - 8 = -1$ ;  $\text{Cl: } 7 - 7 = 0$ . The sum of the formal charges of all the atoms equals  $-1$ , which is identical to the charge of the ion  $(-1)$ .

#### Check Your Learning

Calculate the formal charge for each atom in the carbon monoxide molecule:



**Note:**

**Answer:**

C -1, O +1

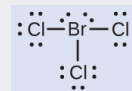
**Example:**

### Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule  $\text{BrCl}_3$ .

**Solution**

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge: Br:  $7 - 7 = 0$  Cl:  $7 - 7 = 0$  All three atoms have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

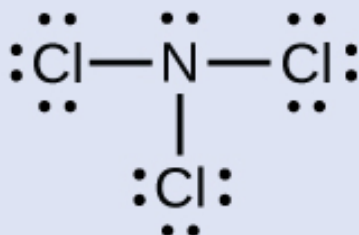
### Check Your Learning

Determine the formal charge for each atom in  $\text{NCl}_3$ .

**Note:**

**Answer:**

N: 0; all three Cl atoms: 0



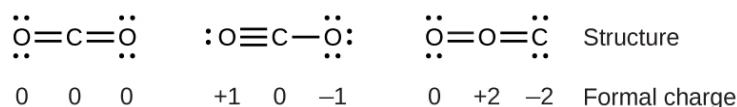


## Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

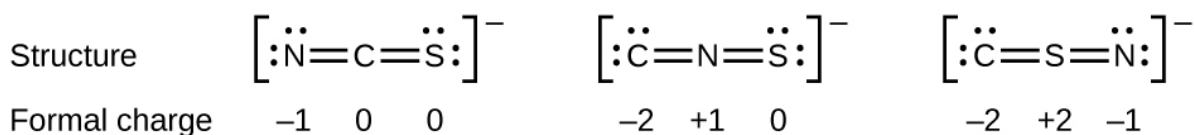
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide,  $\text{CO}_2$ . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures:  $\text{NCS}^-$ ,  $\text{CNS}^-$ , or  $\text{CSN}^-$ . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

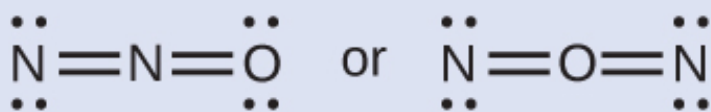


Note that the sum of the formal charges in each case is equal to the charge of the ion ( $-1$ ). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

### Example:

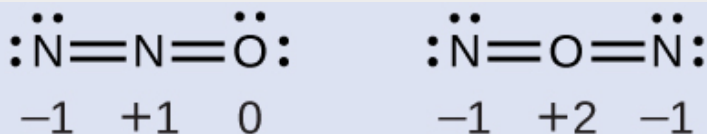
#### Using Formal Charge to Determine Molecular Structure

Nitrous oxide,  $\text{N}_2\text{O}$ , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



**Solution**

Determining formal charge yields the following:



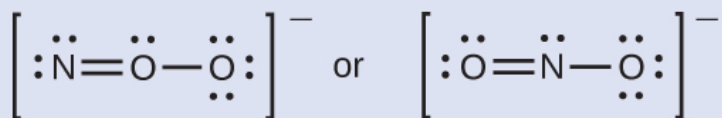
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

**Check Your Learning**

Which is the most likely molecular structure for the nitrite ( $\text{NO}_2^-$ ) ion?

**Note:****Answer:**

$\text{ONO}^-$

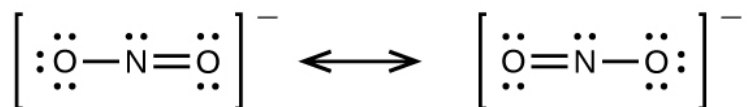
**Resonance**

Notice that the more likely structure for the nitrite anion in [\[link\]](#) may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:



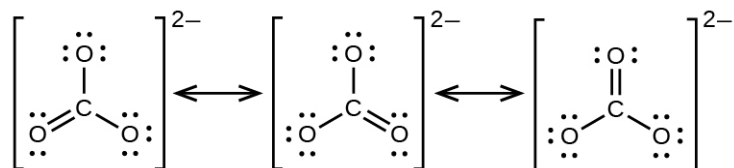
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N-O bonds in  $\text{NO}_2^-$  have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for  $\text{NO}_2^-$  in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in  $\text{NO}_2^-$  is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion,  $\text{CO}_3^{2-}$ , provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

**Note:**

The online [Lewis Structure Make](#) includes many examples to practice drawing resonance structures.

## Key Concepts and Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

## Key Equations

---

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ one pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

---

## Chemistry End of Chapter Exercises

### Exercise:

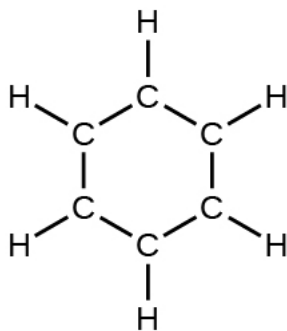
**Problem:** Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) selenium dioxide,  $\text{OSeO}$

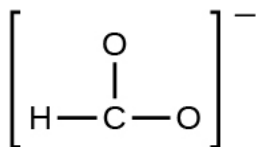
(b) nitrate ion,  $\text{NO}_3^-$

(c) nitric acid,  $\text{HNO}_3$  (N is bonded to an OH group and two O atoms)

(d) benzene,  $\text{C}_6\text{H}_6$ :



(e) the formate ion:



### Exercise:

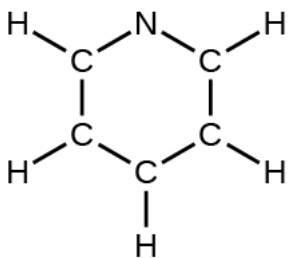
**Problem:** Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) sulfur dioxide,  $\text{SO}_2$

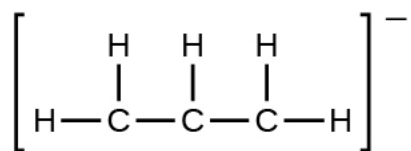
(b) carbonate ion,  $\text{CO}_3^{2-}$

(c) hydrogen carbonate ion,  $\text{HCO}_3^-$  (C is bonded to an OH group and two O atoms)

(d) pyridine:

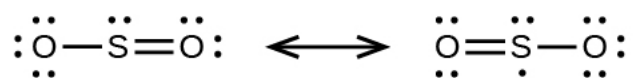


(e) the allyl ion:

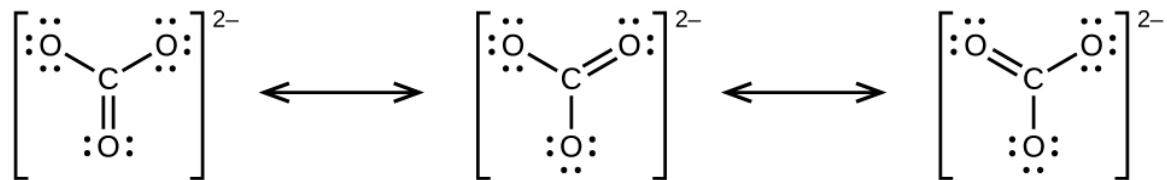


**Solution:**

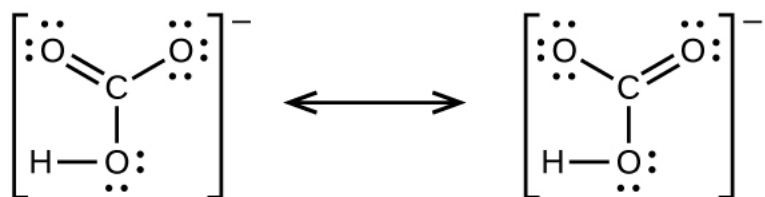
(a)



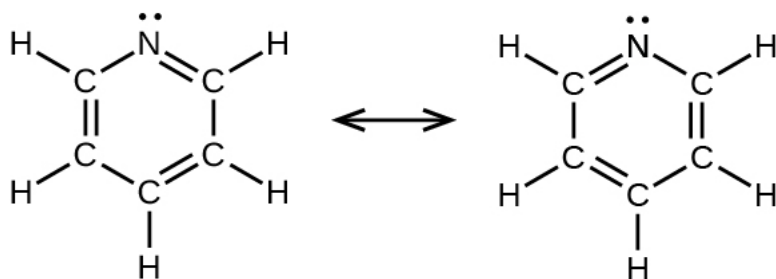
(b)



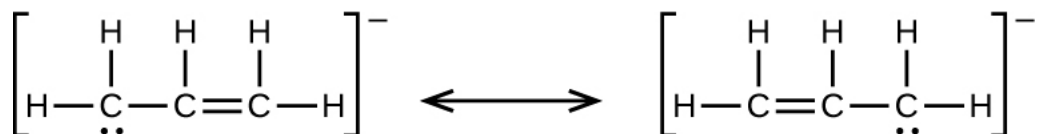
(c)



(d)



(e)



**Exercise:**

**Problem:**

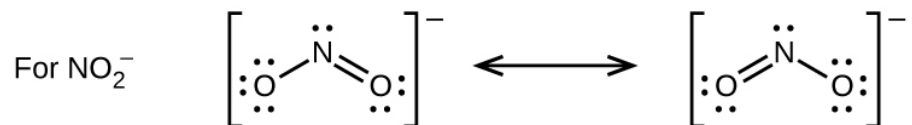
Write the resonance forms of ozone,  $\text{O}_3$ , the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

**Exercise:**

**Problem:**

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion,  $\text{NO}_2^-$ .

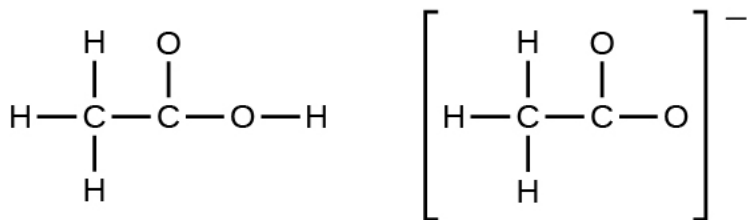
**Solution:**



**Exercise:**

**Problem:**

In terms of the bonds present, explain why acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



**Exercise:****Problem:**

Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

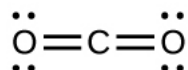
(a)  $\text{CO}_2$

(b)  $\text{CO}$

---

**Solution:**

(a)



(b)



$\text{CO}$  has the strongest carbon-oxygen bond because there is a triple bond joining C and O.  $\text{CO}_2$  has double bonds.

**Exercise:****Problem:**

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

**Exercise:**

**Problem:** Determine the formal charge of each element in the following:

(a)  $\text{HCl}$

(b)  $\text{CF}_4$

(c)  $\text{PCl}_3$

(d)  $\text{PF}_5$

---

**Solution:**

(a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl: 0; (d) P: 0, F: 0

**Exercise:**

**Problem:** Determine the formal charge of each element in the following:

(a)  $\text{H}_3\text{O}^+$

(b)  $\text{SO}_4^{2-}$

(c)  $\text{NH}_3$

(d)  $\text{O}_2^{2-}$

(e)  $\text{H}_2\text{O}_2$

**Exercise:**

**Problem:** Calculate the formal charge of chlorine in the molecules  $\text{Cl}_2$ ,  $\text{BeCl}_2$ , and  $\text{ClF}_5$ .

---

**Solution:**

Cl in  $\text{Cl}_2$ : 0; Cl in  $\text{BeCl}_2$ : 0; Cl in  $\text{ClF}_5$ : 0

**Exercise:**

**Problem:** Calculate the formal charge of each element in the following compounds and ions:

(a)  $\text{F}_2\text{CO}$

(b)  $\text{NO}^-$

(c)  $\text{BF}_4^-$

(d)  $\text{SnCl}_3^-$

(e)  $\text{H}_2\text{CCH}_2$

(f)  $\text{ClF}_3$

(g)  $\text{SeF}_6$

(h)  $\text{PO}_4^{3-}$

**Exercise:**

**Problem:**

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

(a)  $\text{O}_3$

(b)  $\text{SO}_2$

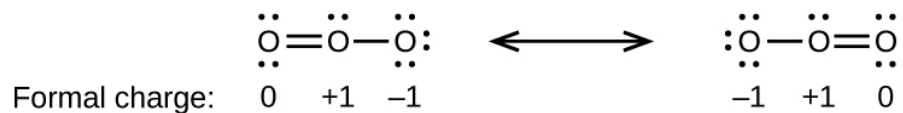
(c)  $\text{NO}_2^-$

(d)  $\text{NO}_3^-$

---

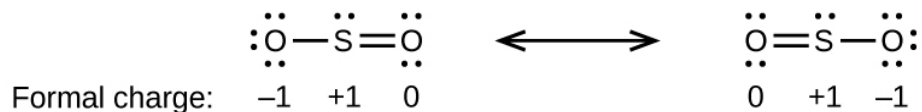
**Solution:**

(a)

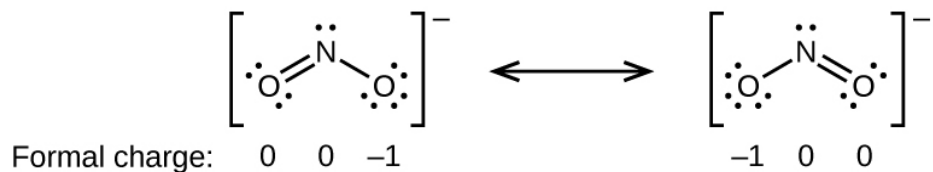


(b)

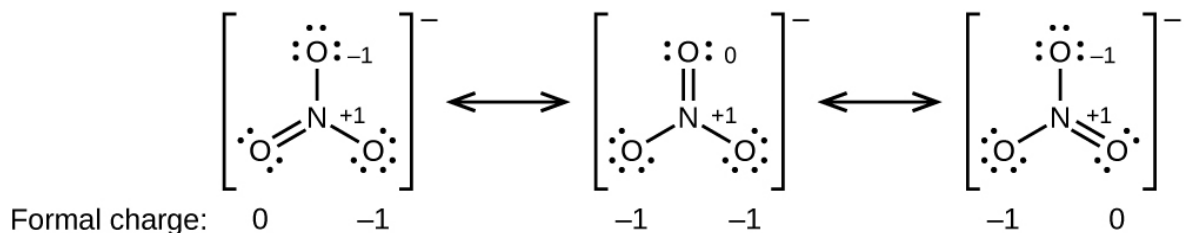




(c)



(d)



**Exercise:**

**Problem:**

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

**Exercise:**

**Problem:**

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

**Solution:**

HOCl

**Exercise:**

**Problem:**

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

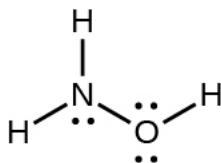
**Exercise:**

**Problem:**

Draw the structure of hydroxylamine,  $\text{H}_3\text{NO}$ , and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

**Solution:**

The structure that gives zero formal charges is consistent with the actual structure:



**Exercise:**

**Problem:**

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

(a) IF

(b) IF<sub>3</sub>

(c) IF<sub>5</sub>

(d) IF<sub>7</sub>

**Exercise:**

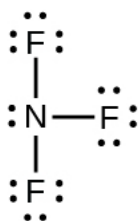
**Problem:**

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

---

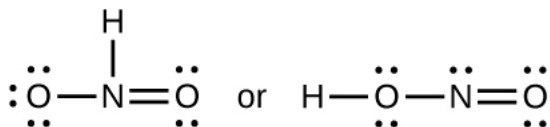
**Solution:**

NF<sub>3</sub>;



**Exercise:**

**Problem:** Which of the following structures would we expect for nitrous acid? Determine the formal charges:

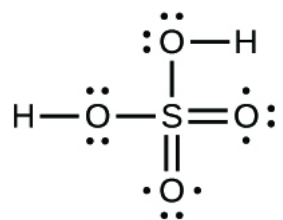


**Exercise:**

**Problem:**

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid,  $\text{H}_2\text{SO}_4$ , which has two oxygen atoms and two OH groups bonded to the sulfur.

---

**Solution:****Glossary****formal charge**

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

**molecular structure**

arrangement of atoms in a molecule or ion

**resonance**

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

**resonance forms**

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

**resonance hybrid**

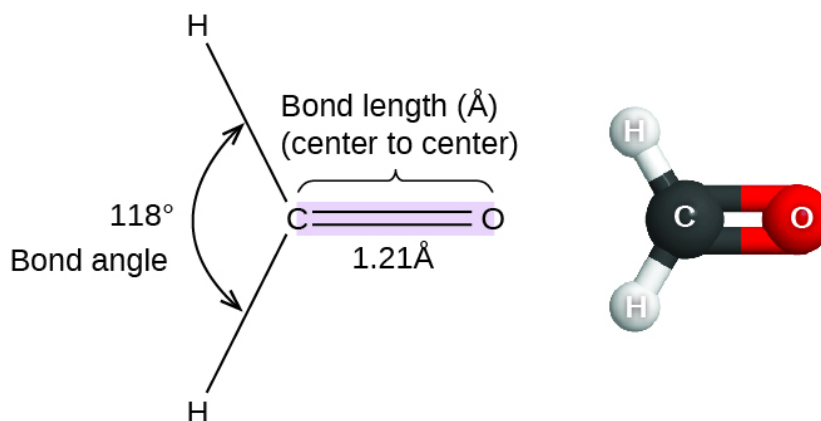
average of the resonance forms shown by the individual Lewis structures

## Molecular Structure and Polarity

By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space ([\[link\]](#)). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms ( $1 \text{ Å} = 10^{-10} \text{ m}$ ) or picometers ( $1 \text{ pm} = 10^{-12} \text{ m}$ ,  $100 \text{ pm} = 1 \text{ Å}$ ).



Bond distances (lengths) and angles are shown for the formaldehyde molecule, H<sub>2</sub>CO.

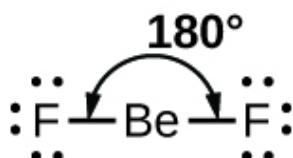
## VSEPR Theory

**Valence shell electron-pair repulsion theory (VSEPR theory)** enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that

electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

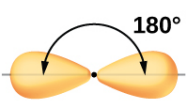
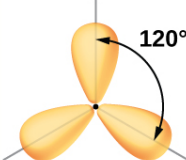
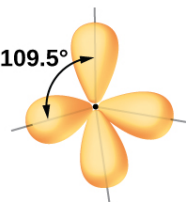
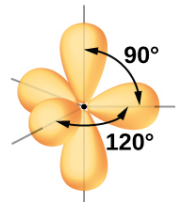
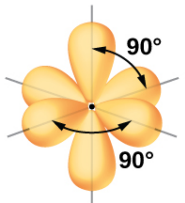
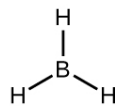
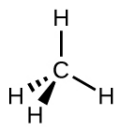
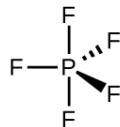
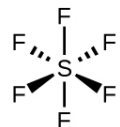
As a simple example of VSEPR theory, let us predict the structure of a gaseous  $\text{BeF}_2$  molecule. The Lewis structure of  $\text{BeF}_2$  ([\[link\]](#)) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is  $180^\circ$  ([\[link\]](#)).



The  $\text{BeF}_2$  molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

[\[link\]](#) illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a

**linear** geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	<chem>H-Be-H</chem>				
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

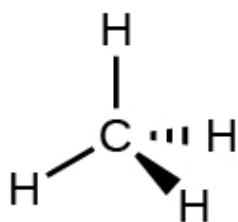
The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

## Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in [\[link\]](#) describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

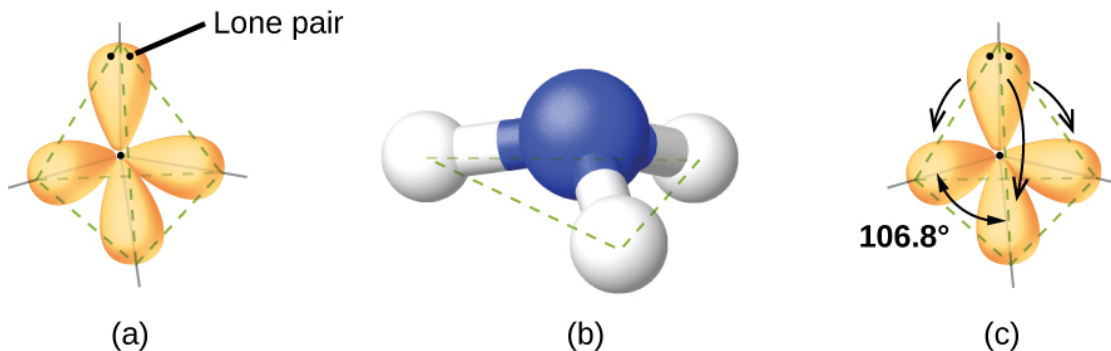
For example, the methane molecule,  $\text{CH}_4$ , which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure ([\[link\]](#)). On the other hand, the ammonia molecule,  $\text{NH}_3$ , also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule ([\[link\]](#)).



The  
molecular  
structure of  
the methane  
molecule,  
 $\text{CH}_4$ , is  
shown with

a  
tetrahedral  
arrangement  
of the  
hydrogen  
atoms.  
VSEPR  
structures  
like this one  
are often  
drawn using  
the wedge  
and dash  
notation, in  
which solid  
lines  
represent  
bonds in the  
plane of the  
page, solid  
wedges  
represent  
bonds  
coming up  
out of the  
plane, and  
dashed lines  
represent  
bonds going  
down into  
the plane.





(a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than  $109.5^\circ$ .

As seen in [\[link\]](#), small distortions from the ideal angles in [\[link\]](#) can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

**Equation:**

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

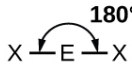
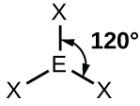
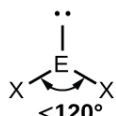
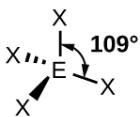


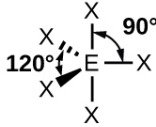
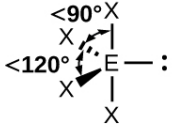
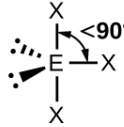
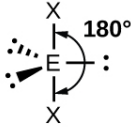
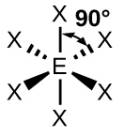
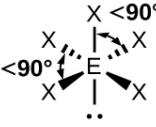
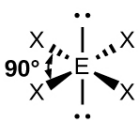
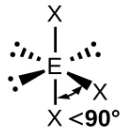
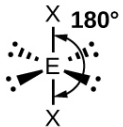
**Equation:**

lone pair > triple bond > double bond > single bond

Consider formaldehyde,  $\text{H}_2\text{CO}$ , which is used as a preservative for biological and anatomical specimens ([\[link\]](#)). This molecule has regions of high electron

density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with  $120^\circ$  bond angles, but we see that the double bond causes slightly larger angles ( $121^\circ$ ), and the angle between the single bonds is slightly smaller ( $118^\circ$ ).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid ([\[link\]](#)) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in  $\text{NH}_3$  are slightly smaller than the  $109.5^\circ$  angle in a regular tetrahedron ([\[link\]](#)) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion ([\[link\]](#)). [\[link\]](#) illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

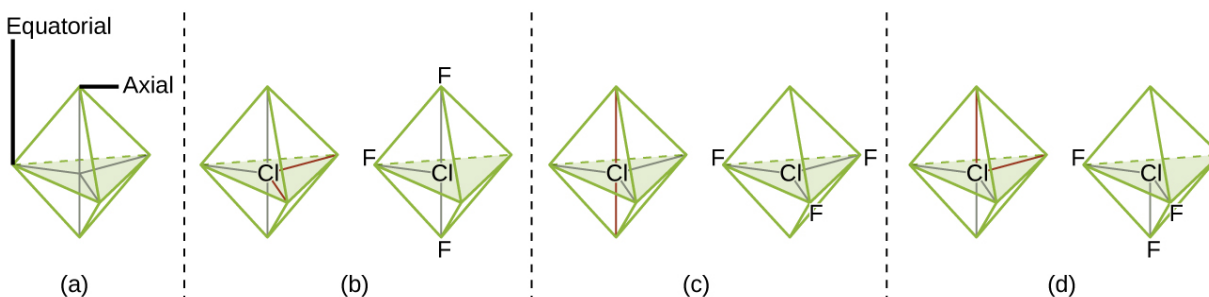
Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in [\[link\]](#)) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in [\[link\]](#): an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis

around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in [\[link\]](#), the axial position is surrounded by bond angles of  $90^\circ$ , whereas the equatorial position has more space available because of the  $120^\circ$  bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the  $\text{ClF}_3$  molecule ([\[link\]](#)). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.



(a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in  $\text{ClF}_3$  have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron ( $180^\circ$  apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions ([\[link\]](#)).

## Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral ([link](#), first column).
4. Use the number of lone pairs to determine the molecular structure ([link](#)). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

**Example:**

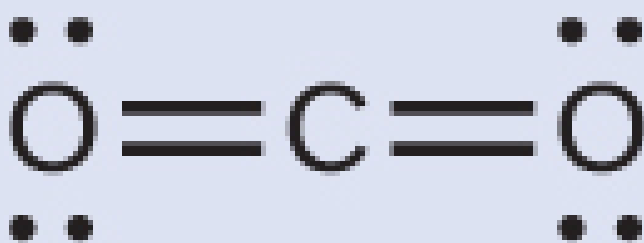
**Predicting Electron-pair Geometry and Molecular Structure:  $\text{CO}_2$  and  $\text{BCl}_3$**

Predict the electron-pair geometry and molecular structure for each of the following:

- (a) carbon dioxide,  $\text{CO}_2$ , a molecule produced by the combustion of fossil fuels
- (b) boron trichloride,  $\text{BCl}_3$ , an important industrial chemical

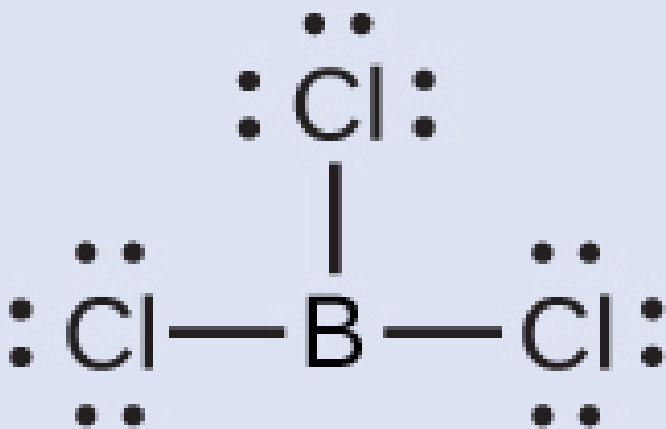
**Solution**

- (a) We write the Lewis structure of  $\text{CO}_2$  as:

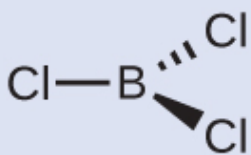


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of  $180^\circ$ . The electron-pair geometry and molecular structure are identical, and  $\text{CO}_2$  molecules are linear.

(b) We write the Lewis structure of  $\text{BCl}_3$  as:



Thus we see that  $\text{BCl}_3$  contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The  $\text{B}-\text{Cl}$  bonds lie in a plane with  $120^\circ$  angles between them.  $\text{BCl}_3$  also has a trigonal planar molecular structure ([link](#)).



The electron-pair geometry and molecular structure of  $\text{BCl}_3$  are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles ( $120^\circ$ ),

unlike the Lewis structure shown above.

### Check Your Learning

Carbonate,  $\text{CO}_3^{2-}$ , is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

#### Note:

#### Answer:

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

### Example:

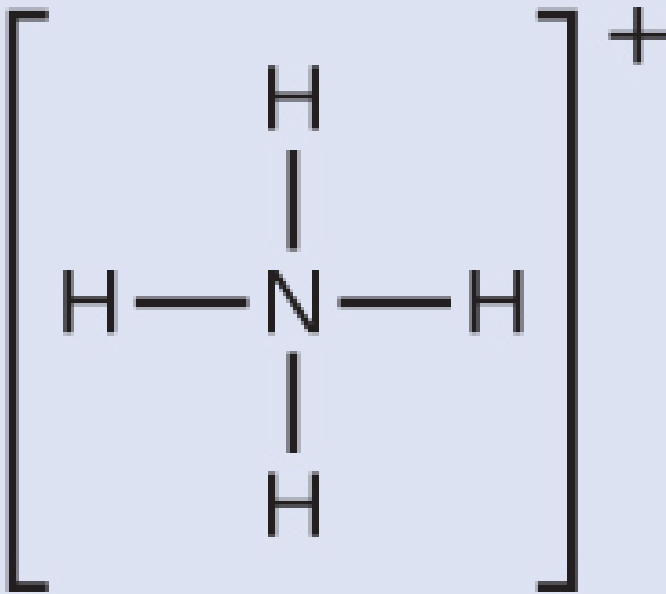
#### Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion.

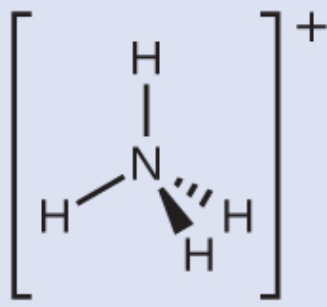
Predict the electron-pair geometry and molecular structure of the  $\text{NH}_4^+$  cation.

#### Solution

We write the Lewis structure of  $\text{NH}_4^+$  as:



We can see that  $\text{NH}_4^+$  contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle ([link](#)). Therefore, the electron pair geometry of  $\text{NH}_4^+$  is tetrahedral, and the molecular structure is also tetrahedral ([link](#)).



The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.



**Check Your Learning**

Identify a molecule with trigonal bipyramidal molecular structure.

**Note:****Answer:**

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal.  $\text{PF}_5$  is a common example.

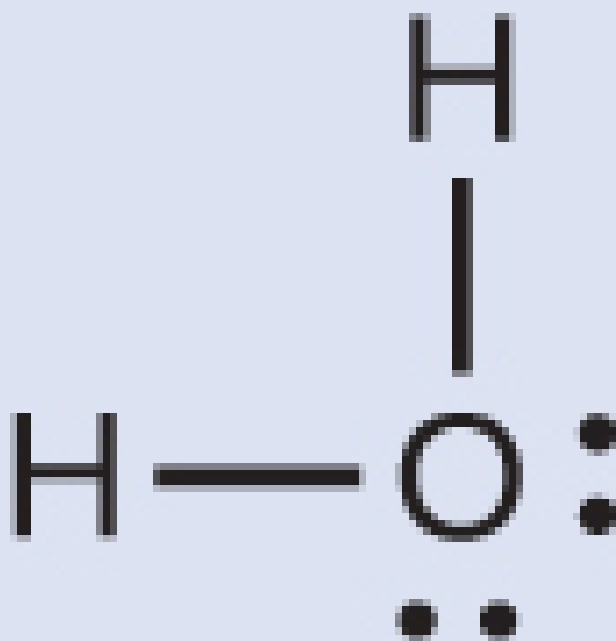
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

**Example:****Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom**

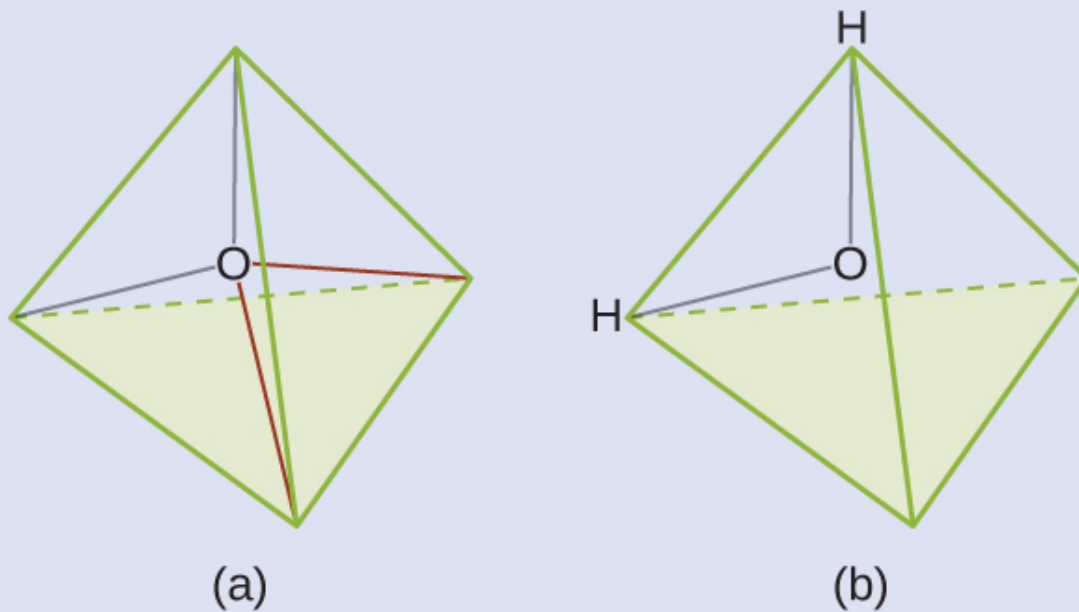
Predict the electron-pair geometry and molecular structure of a water molecule.

**Solution**

The Lewis structure of  $\text{H}_2\text{O}$  indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion ([\[link\]](#)), as indicated in [\[link\]](#). Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than  $109.5^\circ$ . In fact, the bond angle is  $104.5^\circ$ .



(a)  $\text{H}_2\text{O}$  has four regions of electron density around the central atom, so it

has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

**Check Your Learning**

The hydronium ion,  $\text{H}_3\text{O}^+$ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

**Note:****Answer:**

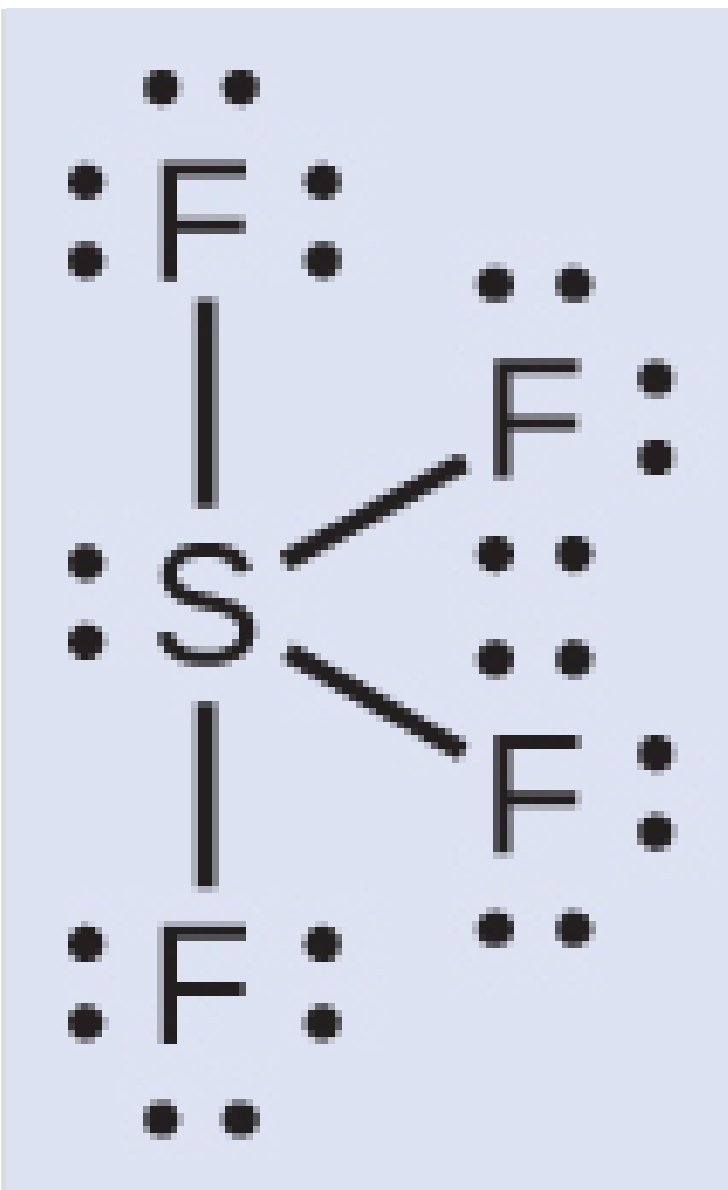
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

**Example:****Predicting Electron-pair Geometry and Molecular Structure:  $\text{SF}_4$** 

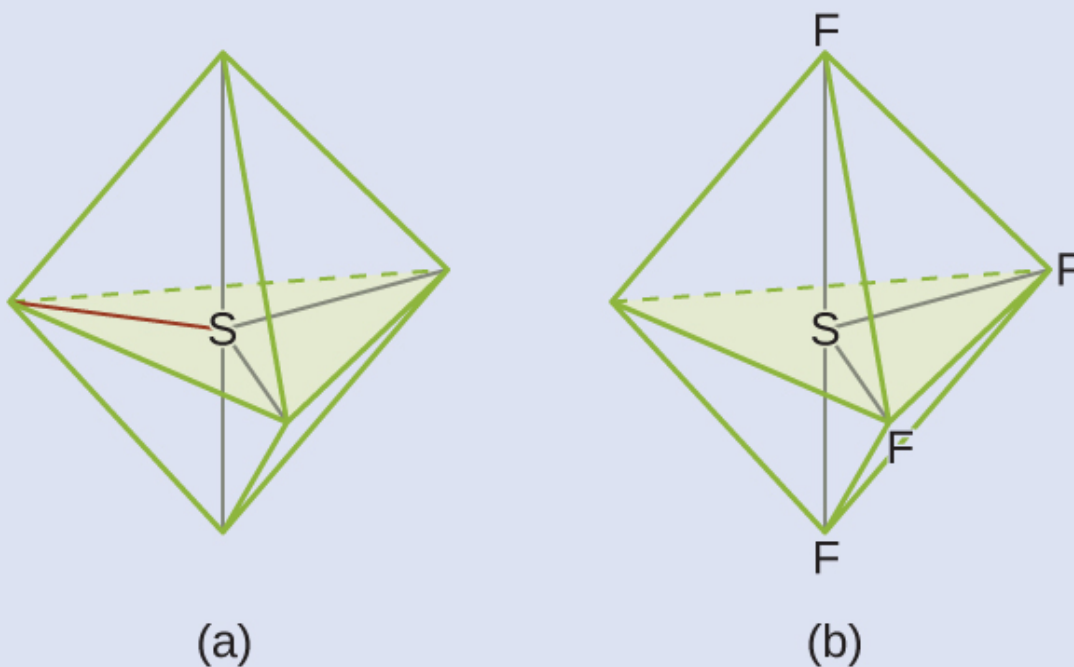
Sulfur tetrafluoride,  $\text{SF}_4$ , is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e.,  $\text{SF}_4$  is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a  $\text{SF}_4$  molecule.

**Solution**

The Lewis structure of  $\text{SF}_4$  indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure ([\[link\]](#)) is that of a seesaw ([\[link\]](#)).



(a) SF<sub>4</sub> has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

### Check Your Learning

Predict the electron pair geometry and molecular structure for molecules of XeF<sub>2</sub>.

**Note:**

**Answer:**

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

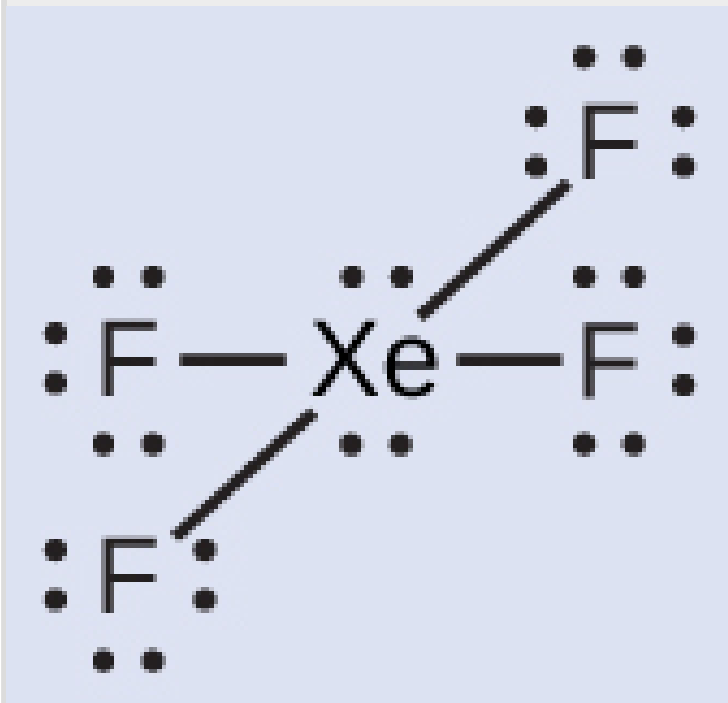
**Example:**

### Predicting Electron-pair Geometry and Molecular Structure: XeF<sub>4</sub>

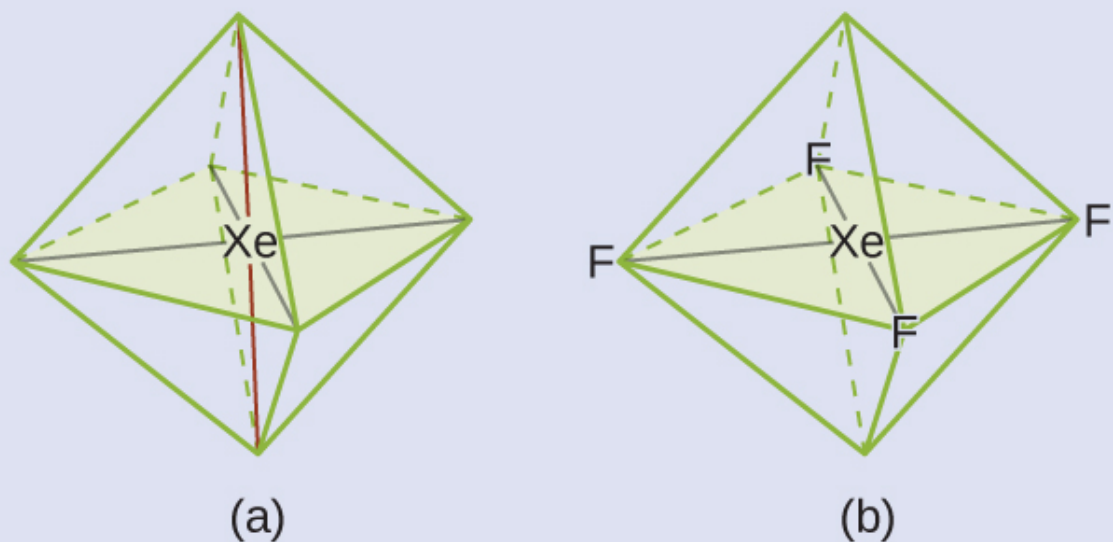
Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF<sub>4</sub> molecule.

#### Solution

The Lewis structure of XeF<sub>4</sub> indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement ([\[link\]](#)), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom ([\[link\]](#)). The five atoms are all in the same plane and have a square planar molecular structure.



(a)  $\text{XeF}_4$  adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

### Check Your Learning

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

**Note:**

**Answer:**

electron pair geometry: trigonal bipyramidal; molecular structure: linear

### Molecular Structure for Multicenter Molecules

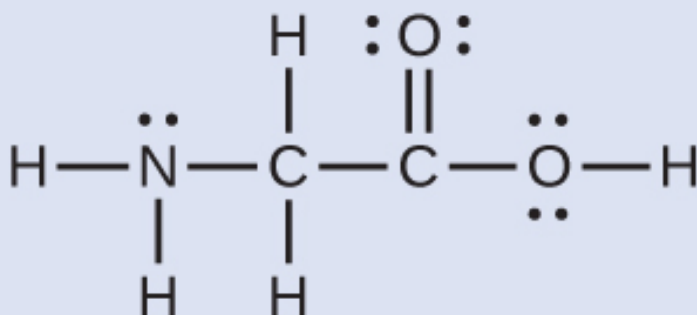
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a “local” geometry. The way these local structures are oriented

with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

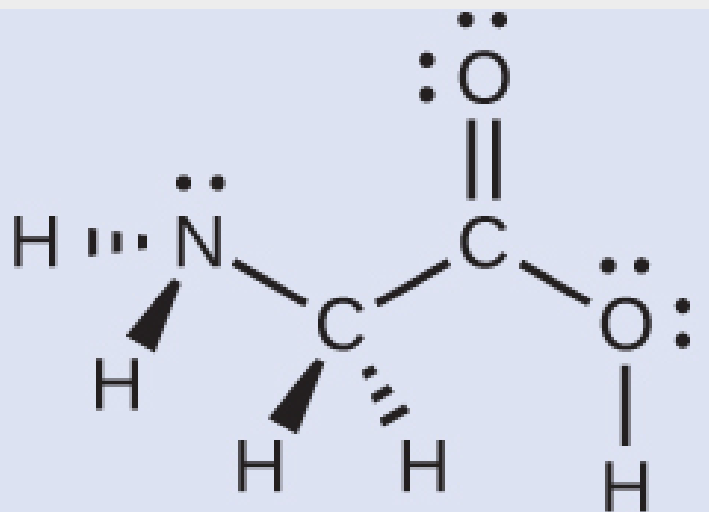
**Example:**

**Predicting Structure in Multicenter Molecules**

The Lewis structure for the simplest amino acid, glycine,  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ , is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



**Solution**



Consider each central atom independently. The electron-pair geometries:

- nitrogen—four regions of electron density; tetrahedral
- carbon ( $\text{CH}_2$ )—four regions of electron density; tetrahedral



- carbon ( $\underline{\text{C}}\text{O}_2$ )—three regions of electron density; trigonal planar
- oxygen ( $\underline{\text{O}}\text{H}$ )—four regions of electron density; tetrahedral

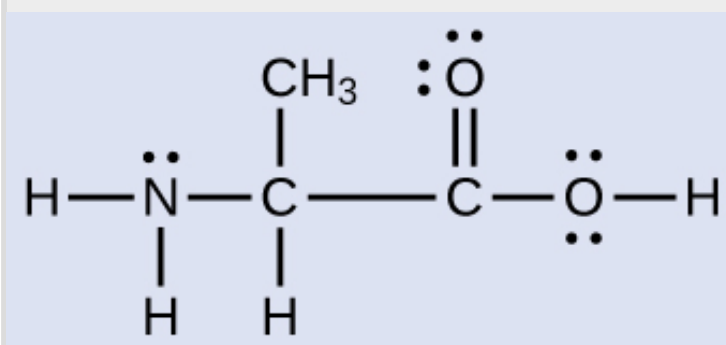
The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ( $\underline{\text{C}}\text{H}_2$ )—four bonds, no lone pairs; tetrahedral
- carbon ( $\underline{\text{C}}\text{O}_2$ )—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ( $\underline{\text{O}}\text{H}$ )—two bonds, two lone pairs; bent ( $109^\circ$ )

### Check Your Learning

Another amino acid is alanine, which has the Lewis structure shown here.

Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



#### Note:

#### Answer:

electron-pair geometries: nitrogen—tetrahedral; carbon ( $\underline{\text{C}}\text{H}$ )—tetrahedral; carbon ( $\underline{\text{C}}\text{H}_3$ )—tetrahedral; carbon ( $\underline{\text{C}}\text{O}_2$ )—trigonal planar; oxygen ( $\underline{\text{O}}\text{H}$ )—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ( $\underline{\text{C}}\text{H}$ )—tetrahedral; carbon ( $\underline{\text{C}}\text{H}_3$ )—tetrahedral; carbon ( $\underline{\text{C}}\text{O}_2$ )—trigonal planar; oxygen ( $\underline{\text{O}}\text{H}$ )—bent ( $109^\circ$ )

#### Note:

The [molecular shape simulator](#) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

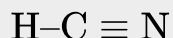
**Example:**

**Molecular Simulation**

Using [molecular shape simulator](#) allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

**Equation:**



Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

**Solution**

The molecular structure is linear.

**Check Your Learning**

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

**Note:**

**Answer:**

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure.  $\text{XeOF}_4$  is a molecule that adopts this structure.

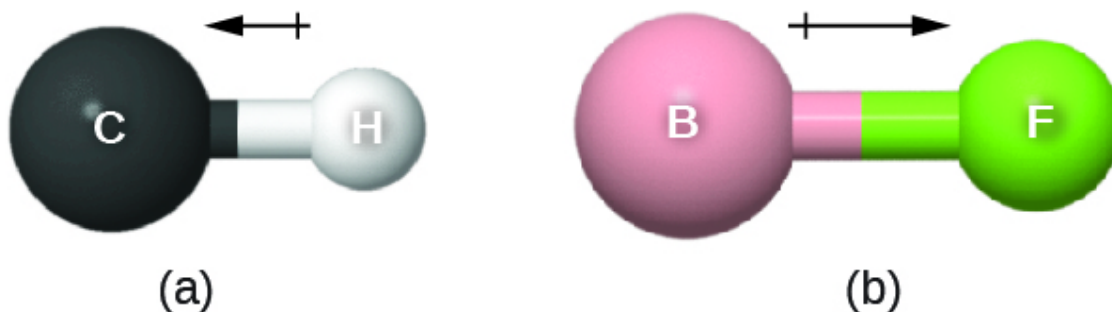
## Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge ( $\delta^+$ ) and the other atom with a partial negative charge ( $\delta^-$ ), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu ( $\mu$ ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

**Equation:**

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude ([\[link\]](#)). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end of the bond to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

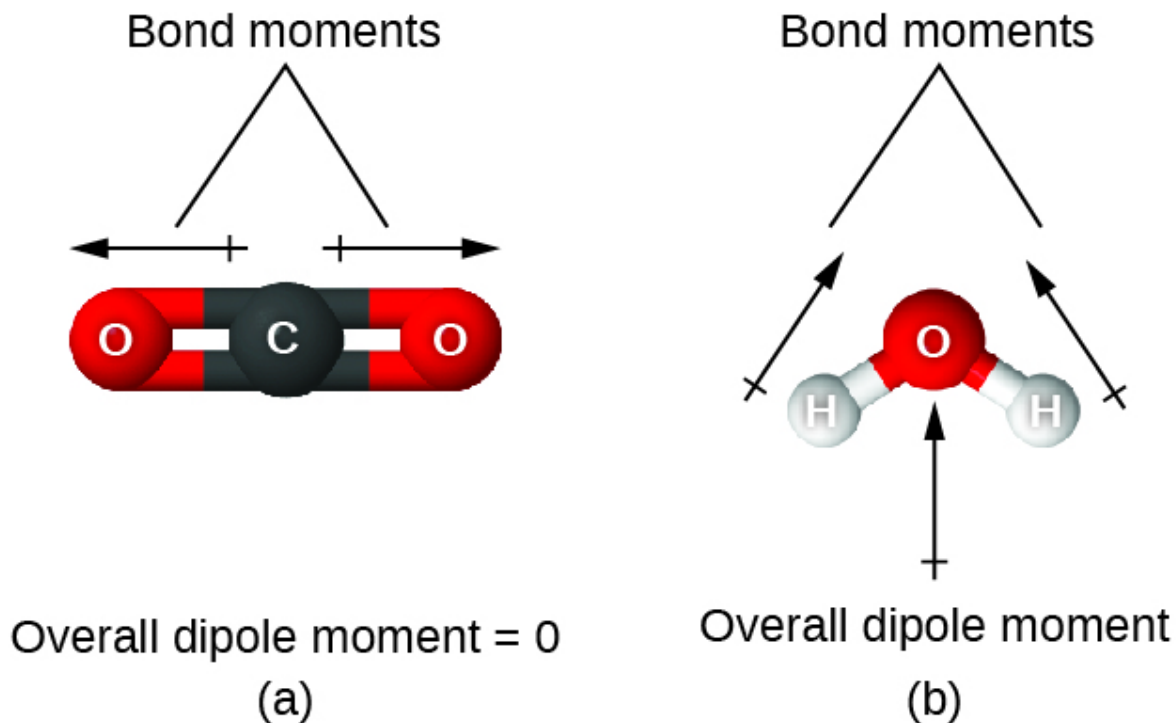


(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as  $\text{Br}_2$  and  $\text{N}_2$  have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as  $\text{CO}$ , there is a small dipole moment. For  $\text{HF}$ , there is a larger dipole moment because there is a larger difference in electronegativity.

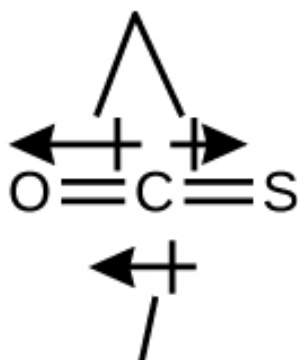
When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in  $\text{CO}_2$  ([\[link\]](#)). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the  $\text{CO}_2$  molecule is linear with polar  $\text{C}=\text{O}$  bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule ([\[link\]](#)), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).



The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO<sub>2</sub> molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO<sub>2</sub>, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

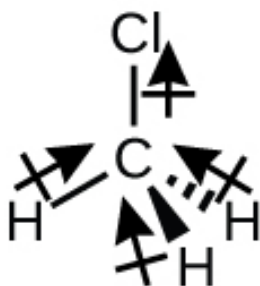
## Bond moments



## Overall dipole moment

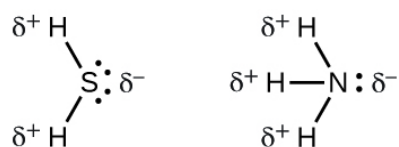
The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane,  $\text{CH}_3\text{Cl}$ , is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is  $\text{H} < \text{C} < \text{Cl}$ , and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



For molecules of high symmetry such as  $\text{BF}_3$  (trigonal planar),  $\text{CH}_4$  (tetrahedral),  $\text{PF}_5$  (trigonal bipyramidal), and  $\text{SF}_6$  (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of

such molecules include hydrogen sulfide,  $\text{H}_2\text{S}$  (nonlinear), and ammonia,  $\text{NH}_3$  (trigonal pyramidal).

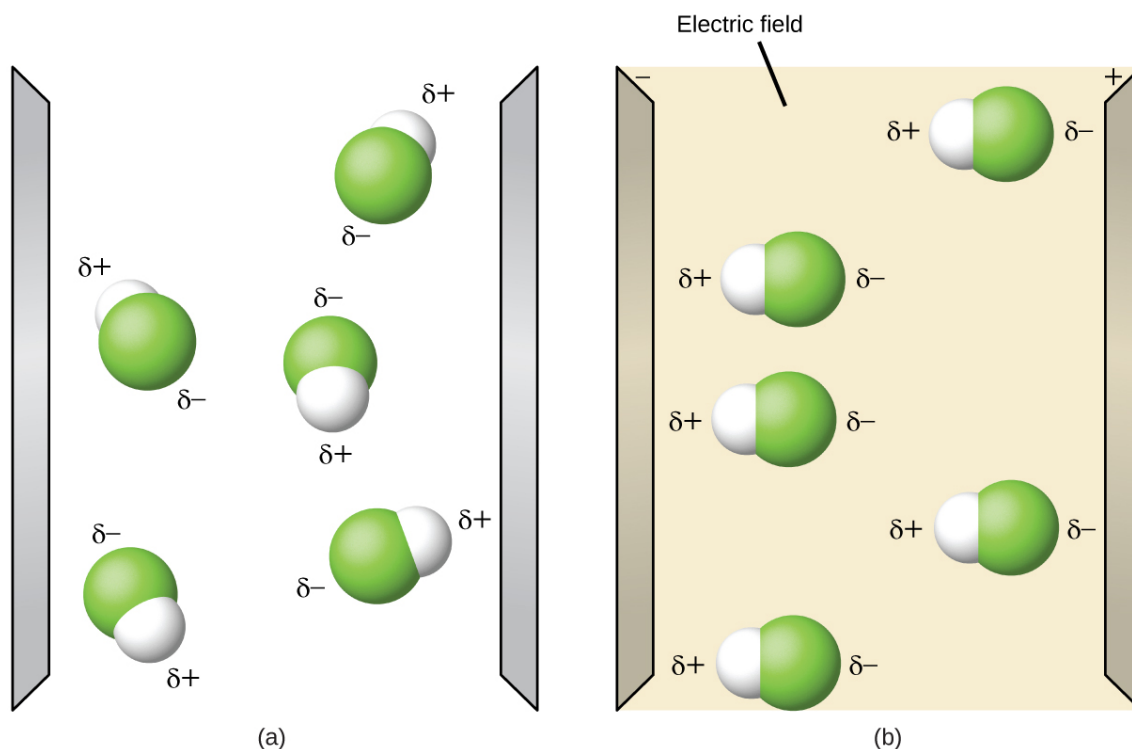


To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

## Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate ([\[link\]](#)). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.



(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

**Note:**

The [molecule polarity simulation](#) provides many ways to explore dipole moments of bonds and molecules.

**Example:**

**Polarity Simulations**

Open the [molecule polarity simulation](#) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjusters. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to [\[link\]](#).



Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

- (a) A and C are very electronegative and B is in the middle of the range.
- (b) A is very electronegative, and B and C are not.

**Solution**

- (a) Molecular dipole moment points immediately between A and C.
- (b) Molecular dipole moment points along the A–B bond, toward A.

**Check Your Learning**

Determine the partial charges that will give the largest possible bond dipoles.

**Note:**

**Answer:**

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

## Key Concepts and Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar

molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

---

#### Solution:

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

### Exercise:

#### Problem:

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

### Exercise:

#### Problem:

Explain the difference between electron-pair geometry and molecular structure.

---

#### Solution:

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

### Exercise:

**Problem:**

Why is the H–N–H angle in  $\text{NH}_3$  smaller than the H–C–H bond angle in  $\text{CH}_4$ ? Why is the H–N–H angle in  $\text{NH}_4^+$  identical to the H–C–H bond angle in  $\text{CH}_4$ ?

**Exercise:****Problem:**

Explain how a molecule that contains polar bonds can be nonpolar.

---

**Solution:**

As long as the polar bonds are compensated (for example, two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

**Exercise:****Problem:**

As a general rule,  $\text{MX}_n$  molecules (where M represents a central atom and X represents terminal atoms;  $n = 2 - 5$ ) are polar if there is one or more lone pairs of electrons on M.  $\text{NH}_3$  (M = N, X = H,  $n = 3$ ) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

**Exercise:****Problem:**

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a)  $\text{SF}_6$

(b)  $\text{PCl}_5$

(c)  $\text{BeH}_2$

(d)  $\text{CH}_3^+$

---

**Solution:**

(a) Both the electron geometry and the molecular structure are octahedral.  
(b) Both the electron geometry and the molecular structure are trigonal bipyramidal.  
(c) Both the electron geometry and the molecular structure are linear.  
(d) Both the electron geometry and the molecular structure are trigonal planar.

**Exercise:****Problem:**

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

- (a)  $\text{IF}_6^+$
- (b)  $\text{CF}_4$
- (c)  $\text{BF}_3$
- (d)  $\text{SiF}_5^-$
- (e)  $\text{BeCl}_2$

**Exercise:****Problem:**

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

- (a)  $\text{ClF}_5$
- (b)  $\text{ClO}_2^-$
- (c)  $\text{TeCl}_4^{2-}$
- (d)  $\text{PCl}_3$
- (e)  $\text{SeF}_4$
- (f)  $\text{PH}_2^-$

---

**Solution:**

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent ( $109^\circ$ )

**Exercise:****Problem:**

Predict the electron pair geometry and the molecular structure of each of the following ions:

- (a)  $\text{H}_3\text{O}^+$
- (b)  $\text{PCl}_4^-$
- (c)  $\text{SnCl}_3^-$
- (d)  $\text{BrCl}_4^-$
- (e)  $\text{ICl}_3$
- (f)  $\text{XeF}_4$
- (g)  $\text{SF}_2$

**Exercise:****Problem:**

Identify the electron pair geometry and the molecular structure of each of the following molecules:

- (a)  $\text{ClNO}$  (N is the central atom)
- (b)  $\text{CS}_2$

- (c)  $\text{Cl}_2\text{CO}$  (C is the central atom)
  - (d)  $\text{Cl}_2\text{SO}$  (S is the central atom)
  - (e)  $\text{SO}_2\text{F}_2$  (S is the central atom)
  - (f)  $\text{XeO}_2\text{F}_2$  (Xe is the central atom)
  - (g)  $\text{ClOF}_2^+$  (Cl is the central atom)
- 

**Solution:**

(a) electron-pair geometry: trigonal planar, molecular structure: bent ( $120^\circ$ ); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

**Exercise:**

**Problem:**

Predict the electron pair geometry and the molecular structure of each of the following:

- (a)  $\text{IOF}_5$  (I is the central atom)
- (b)  $\text{POCl}_3$  (P is the central atom)
- (c)  $\text{Cl}_2\text{SeO}$  (Se is the central atom)
- (d)  $\text{ClSO}^+$  (S is the central atom)
- (e)  $\text{F}_2\text{SO}$  (S is the central atom)
- (f)  $\text{NO}_2^-$
- (g)  $\text{SiO}_4^{4-}$

**Exercise:**

**Problem:**

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

- (a)  $\text{ClF}_5$
  - (b)  $\text{ClO}_2^-$
  - (c)  $\text{TeCl}_4^{2-}$
  - (d)  $\text{PCl}_3$
  - (e)  $\text{SeF}_4$
  - (f)  $\text{PH}_2^-$
  - (g)  $\text{XeF}_2$
- 

**Solution:**

All of these molecules and ions contain polar bonds. Only  $\text{ClF}_5$ ,  $\text{ClO}_2^-$ ,  $\text{PCl}_3$ ,  $\text{SeF}_4$ , and  $\text{PH}_2^-$  have dipole moments.

**Exercise:****Problem:**

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

- (a)  $\text{H}_3\text{O}^+$
- (b)  $\text{PCl}_4^-$
- (c)  $\text{SnCl}_3^-$
- (d)  $\text{BrCl}_4^-$
- (e)  $\text{ICl}_3$
- (f)  $\text{XeF}_4$

(g)  $\text{SF}_2$

**Exercise:**

**Problem:** Which of the following molecules have dipole moments?

(a)  $\text{CS}_2$

(b)  $\text{SeS}_2$

(c)  $\text{CCl}_2\text{F}_2$

(d)  $\text{PCl}_3$  (P is the central atom)

(e)  $\text{ClNO}$  (N is the central atom)

---

**Solution:**

$\text{SeS}_2$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{PCl}_3$ , and  $\text{ClNO}$  all have dipole moments.

**Exercise:**

**Problem:** Identify the molecules with a dipole moment:

(a)  $\text{SF}_4$

(b)  $\text{CF}_4$

(c)  $\text{Cl}_2\text{CCBr}_2$

(d)  $\text{CH}_3\text{Cl}$

(e)  $\text{H}_2\text{CO}$

**Exercise:**

**Problem:**

The molecule  $\text{XF}_3$  has a dipole moment. Is X boron or phosphorus?

---

**Solution:**

P



**Exercise:****Problem:**

The molecule  $\text{XCl}_2$  has a dipole moment. Is X beryllium or sulfur?

**Exercise:**

**Problem:** Is the  $\text{Cl}_2\text{BBCl}_2$  molecule polar or nonpolar?

---

**Solution:**

nonpolar

**Exercise:****Problem:**

There are three possible structures for  $\text{PCl}_2\text{F}_3$  with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

**Exercise:****Problem:**

Describe the molecular structure around the indicated atom or atoms:

- (a) the sulfur atom in sulfuric acid,  $\text{H}_2\text{SO}_4$  [ $(\text{HO})_2\text{SO}_2$ ]
- (b) the chlorine atom in chloric acid,  $\text{HClO}_3$  [ $\text{HOClO}_2$ ]
- (c) the oxygen atom in hydrogen peroxide,  $\text{HOOH}$
- (d) the nitrogen atom in nitric acid,  $\text{HNO}_3$  [ $\text{HONO}_2$ ]
- (e) the oxygen atom in the OH group in nitric acid,  $\text{HNO}_3$  [ $\text{HONO}_2$ ]
- (f) the central oxygen atom in the ozone molecule,  $\text{O}_3$
- (g) each of the carbon atoms in propyne,  $\text{CH}_3\text{CCH}$
- (h) the carbon atom in Freon,  $\text{CCl}_2\text{F}_2$

(i) each of the carbon atoms in allene,  $\text{H}_2\text{CCCH}_2$

---

**Solution:**

(a) tetrahedral; (b) trigonal pyramidal; (c) bent ( $109^\circ$ ); (d) trigonal planar;  
(e) bent ( $109^\circ$ ); (f) bent ( $109^\circ$ ); (g)  $\underline{\text{C}}\text{H}_3\text{CCH}$  tetrahedral,  $\text{CH}_3\underline{\text{C}}\underline{\text{C}}\text{H}$  linear;  
(h) tetrahedral; (i)  $\text{H}_2\underline{\text{C}}\underline{\text{C}}\text{CH}_2$  linear;  $\text{H}_2\underline{\text{C}}\underline{\text{C}}\underline{\text{C}}\text{H}_2$  trigonal planar

**Exercise:**

**Problem:**

Draw the Lewis structures and predict the shape of each compound or ion:

(a)  $\text{CO}_2$

(b)  $\text{NO}_2^-$

(c)  $\text{SO}_3$

(d)  $\text{SO}_3^{2-}$

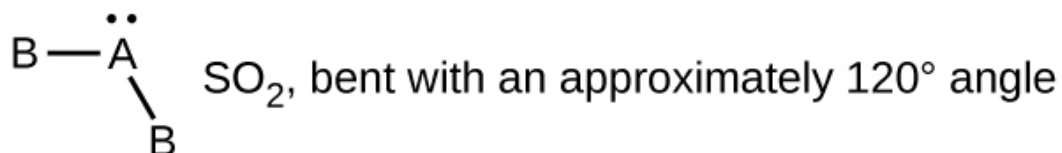
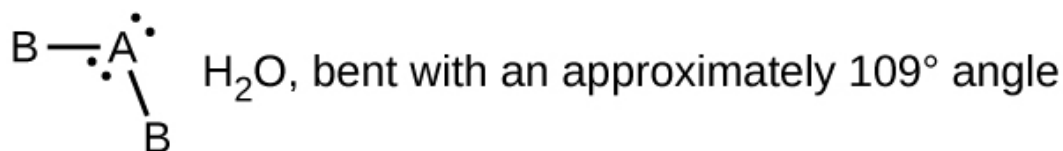
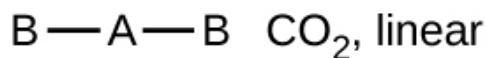
**Exercise:**

**Problem:**

A molecule with the formula  $\text{AB}_2$ , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

---

**Solution:**



**Exercise:**

**Problem:**

A molecule with the formula  $\text{AB}_3$ , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

**Exercise:**

**Problem:**

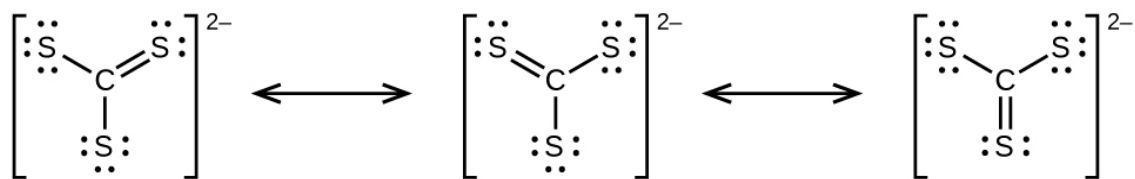
Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:



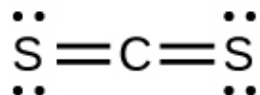
(d) predict the molecular shapes for  $\text{CS}_3^{2-}$  and  $\text{CS}_2$  and explain how you arrived at your predictions

**Solution:**

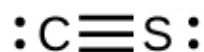
(a)



(b)



(c)



(d)  $\text{CS}_3^{2-}$  includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar;  $\text{CS}_2$  has only two regions of electron density (all bonds with no lone pairs); the shape is linear

### Exercise:

#### Problem:

What is the molecular structure of the stable form of  $\text{FNO}_2$ ? (N is the central atom.)

### Exercise:

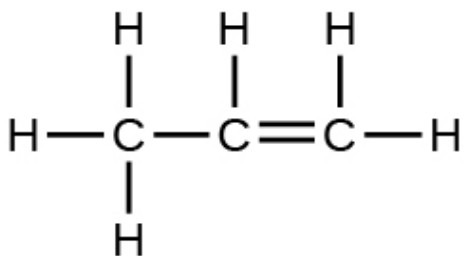
#### Problem:

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

---

#### Solution:

The Lewis structure is made from three units, but the atoms must be rearranged:



**Exercise:**

**Problem:**

Use the [simulation](#) to perform the following exercises for a two-atom molecule:

- Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
- With a partial positive charge on A, turn on the electric field and describe what happens.
- With a small partial negative charge on A, turn on the electric field and describe what happens.
- Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

**Exercise:**

**Problem:**

Use the [simulation](#) to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

- Sketch the bond dipoles and molecular dipole (if any) for  $\text{O}_3$ . Explain your observations.
- Look at the bond dipoles for  $\text{NH}_3$ . Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for  $\text{NH}_3$  and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

---

**Solution:**

The molecular dipole points away from the hydrogen atoms.

**Exercise:**

**Problem:**

Use the [Molecule Shape simulator](#) to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

**Exercise:**

**Problem:**

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select  $\text{H}_2\text{O}$ . Switch between the “real” and “model” modes. Explain the difference observed.

---

**Solution:**

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as  $109.5^\circ$ . In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of  $104.5^\circ$ .

**Exercise:**

**Problem:**

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select “model” mode and  $\text{S}_2\text{O}$ . What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

## Glossary

### axial position

location in a trigonal bipyramidal geometry in which there is another atom at a  $180^\circ$  angle and the equatorial positions are at a  $90^\circ$  angle

### bond angle

angle between any two covalent bonds that share a common atom

### bond distance

(also, bond length) distance between the nuclei of two bonded atoms

### bond dipole moment

separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

### dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

### electron-pair geometry

arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

### equatorial position

one of the three positions in a trigonal bipyramidal geometry with  $120^\circ$  angles between them; the axial positions are located at a  $90^\circ$  angle

### linear

shape in which two outside groups are placed on opposite sides of a central atom

### molecular structure

structure that includes only the placement of the atoms in the molecule

### octahedral

shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a

square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule

(also, dipole) molecule with an overall dipole moment

tetrahedral

shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and  $109.5^\circ$  angles between each pair and the central atom

trigonal bipyramidal

shape in which five outside groups are placed around a central atom such that three form a flat triangle with  $120^\circ$  angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with  $120^\circ$  angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction



## Introduction

class="introduction"

The water in  
a swimming  
pool is a  
complex  
mixture of  
substances  
whose  
relative  
amounts  
must be  
carefully  
maintained  
to ensure  
the health  
and comfort  
of people  
using the  
pool.

(credit:  
modificatio  
n of work  
by Vic  
Brincat)



Swimming pools have long been a popular means of recreation, exercise, and physical therapy. Since it is impractical to refill large pools with fresh water on a frequent basis, pool water is regularly treated with chemicals to prevent the growth of harmful bacteria and algae. Proper pool maintenance requires regular additions of various chemical compounds in carefully measured amounts. For example, the relative amount of calcium ion,  $\text{Ca}^{2+}$ , in the water should be maintained within certain limits to prevent eye irritation and avoid damage to the pool bed and plumbing. To maintain proper calcium levels, calcium cations are added to the water in the form of an ionic compound that also contains anions; thus, it is necessary to know both the relative amount of  $\text{Ca}^{2+}$  in the compound and the volume of water in the pool in order to achieve the proper calcium level. Quantitative aspects of the composition of substances (such as the calcium-containing compound) and mixtures (such as the pool water) are the subject of this chapter.

## Formula Mass

By the end of this section, you will be able to:

- Calculate formula masses for covalent and ionic compounds

Many argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

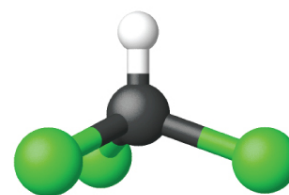
## Formula Mass

An earlier chapter of this text described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

### Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ( $\text{CHCl}_3$ ), a covalent compound once used as a surgical anesthetic and now primarily used in the production of the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. [\[link\]](#) outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

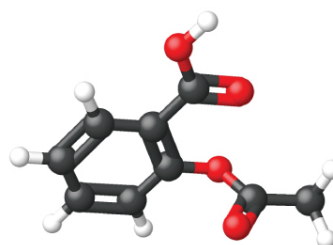
Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
Molecular mass					119.37



The average mass of a chloroform molecule,  $\text{CHCl}_3$ , is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule,  $\text{C}_9\text{H}_8\text{O}_4$ , is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu ([link](#)).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
Molecular mass					180.15



The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin,  $\text{C}_9\text{H}_8\text{O}_4$ .

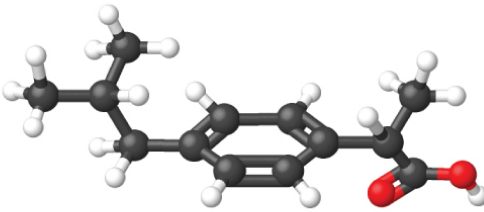
### Example: Computing Molecular Mass for a Covalent Compound

Ibuprofen,  $C_{13}H_{18}O_2$ , is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

### Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.144
O	2	×	16.00	=	32.00
Molecular mass					206.27



### Check Your Learning

Acetaminophen,  $C_8H_9NO_2$ , is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

**Note:**

**Answer:**

151.16 amu

## Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the

atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the “molecular mass.”

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations,  $\text{Na}^+$ , and chloride anions,  $\text{Cl}^-$ , combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see [\[link\]](#)).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
Formula mass					58.44

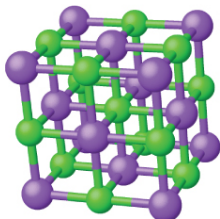


Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chloride anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

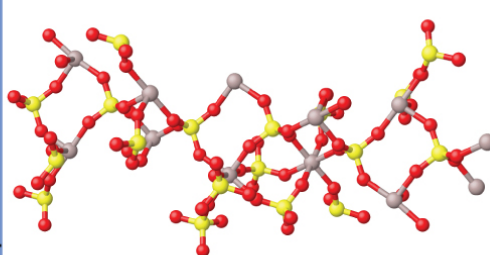
**Example:****Computing Formula Mass for an Ionic Compound**

Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

**Solution**

The formula for this compound indicates it contains  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format,  $\text{Al}_2\text{S}_3\text{O}_{12}$ . Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
Molecular mass					342.14

**Check Your Learning**

Calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

**Note:****Answer:**

310.18 amu

**Key Concepts and Summary**

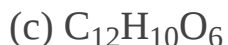
The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one  $\text{H}_2\text{O}$  molecule weighs approximately 18 amu and 1 mole of  $\text{H}_2\text{O}$  molecules weighs approximately 18 g).

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

What is the total mass (amu) of carbon in each of the following molecules?



---

#### Solution:

(a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

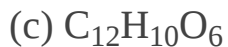
### Exercise:

#### Problem:

What is the total mass of hydrogen in each of the molecules?



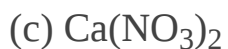




**Exercise:**

**Problem:**

Calculate the molecular or formula mass of each of the following:



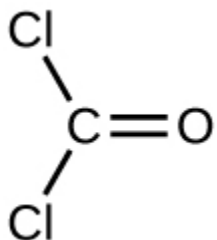
**Solution:**

(a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu;  
(e) 342.297 amu

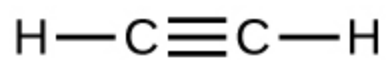
**Exercise:**

**Problem:** Determine the molecular mass of the following compounds:

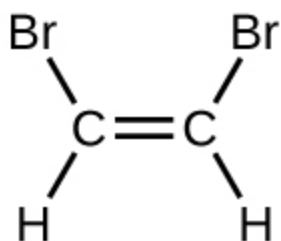
(a)



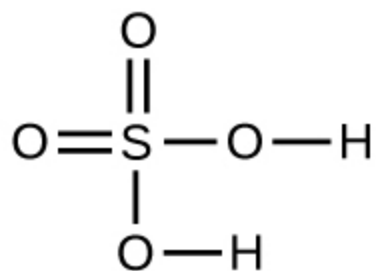
(b)



(c)



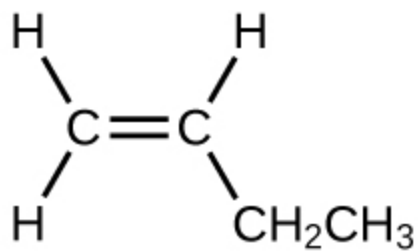
(d)



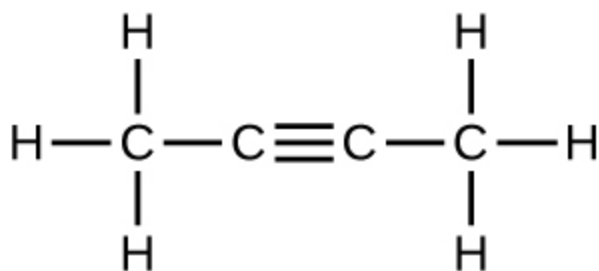
**Exercise:**

**Problem:** Determine the molecular mass of the following compounds:

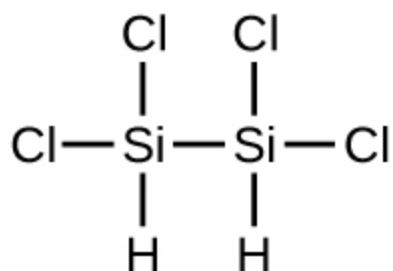
(a)



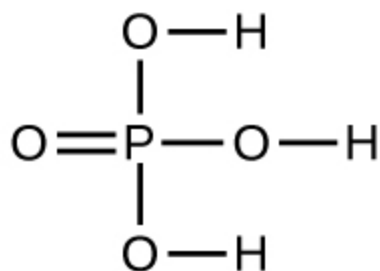
(b)



(c)



(d)



**Solution:**

- (a) 56.107 amu;
- (b) 54.091 amu;
- (c) 199.9976 amu;
- (d) 97.9950 amu

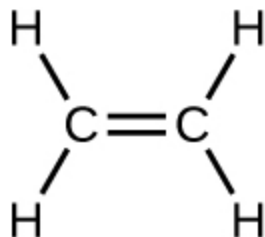
**Exercise:**

**Problem:** Which molecule has a molecular mass of 28.05 amu?

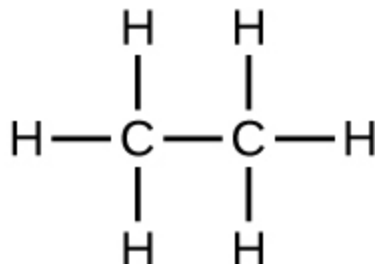
(a)



(b)



(c)



## Glossary

Avogadro's number ( $N_A$ )

experimentally determined value of the number of entities comprising 1 mole of substance, equal to  $6.022 \times 10^{23} \text{ mol}^{-1}$

formula mass

sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

molar mass

mass in grams of 1 mole of a substance

mole

amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of  $^{12}\text{C}$

## Determining Empirical and Molecular Formulas

A previous chapter of this text discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, one may determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, these same principles will be applied to derive the chemical formulas of unknown substances from experimental mass measurements.

### Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's **percent composition**, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

**Equation:**

$$\% \text{ H} = \frac{\text{mass H}}{\text{mass compound}} \times 100 \%$$

**Equation:**

$$\% \text{ C} = \frac{\text{mass C}}{\text{mass compound}} \times 100 \%$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

**Equation:**

$$\% \text{ H} = \frac{2.5 \text{ g H}}{10.0 \text{ g compound}} \times 100 \% = 25 \%$$

**Equation:**

$$\% \text{ C} = \frac{7.5 \text{ g C}}{10.0 \text{ g compound}} \times 100 \% = 75 \%$$

**Example:****Calculation of Percent Composition**

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

**Solution**

To calculate percent composition, divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

**Equation:**

$$\begin{aligned}\% \text{ C} &= \frac{7.34 \text{ g C}}{12.04 \text{ g compound}} \times 100\% = 61.0\% \\ \% \text{ H} &= \frac{1.85 \text{ g H}}{12.04 \text{ g compound}} \times 100\% = 15.4\% \\ \% \text{ N} &= \frac{2.85 \text{ g N}}{12.04 \text{ g compound}} \times 100\% = 23.7\%\end{aligned}$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

**Check Your Learning**

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

**Note:****Answer:**

12.1% C, 16.1% O, 71.8% Cl

**Determining Percent Composition from Molecular or Empirical Formulas**

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia ( $\text{NH}_3$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and urea ( $\text{CH}_4\text{N}_2\text{O}$ ). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For

these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of  $\text{NH}_3$  contains one N atom weighing 14.01 amu and three H atoms weighing a total of  $(3 \times 1.008 \text{ amu}) = 3.024 \text{ amu}$ . The formula mass of ammonia is therefore  $(14.01 \text{ amu} + 3.024 \text{ amu}) = 17.03 \text{ amu}$ , and its percent composition is:

**Equation:**

$$\% \text{ N} = \frac{14.01 \text{ amu N}}{17.03 \text{ amu NH}_3} \times 100 \% = 82.27 \%$$

$$\% \text{ H} = \frac{3.024 \text{ amu H}}{17.03 \text{ amu NH}_3} \times 100 \% = 17.76 \%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated [\[link\]](#). As long as the molecular or empirical formula of the compound in question is known, the percent composition may be derived from the atomic or molar masses of the compound's elements.

**Example:**

**Determining Percent Composition from a Molecular Formula**

Aspirin is a compound with the molecular formula  $\text{C}_9\text{H}_8\text{O}_4$ . What is its percent composition?

**Solution**

To calculate the percent composition, the masses of C, H, and O in a known mass of  $\text{C}_9\text{H}_8\text{O}_4$  are needed. It is convenient to consider 1 mol of  $\text{C}_9\text{H}_8\text{O}_4$  and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

**Equation:**

$$\% \text{ C} = \frac{9 \text{ mol C} \times \text{molar mass C}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 = \frac{9 \times 12.01 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{108.09 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100$$

$$\% \text{ C} = 60.00 \% \text{ C}$$

**Equation:**

$$\% \text{ H} = \frac{8 \text{ mol H} \times \text{molar mass H}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 = \frac{8 \times 1.008 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{8.064 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100$$

$$\% \text{ H} = 4.476 \% \text{ H}$$

**Equation:**

$$\% \text{ O} = \frac{4 \text{ mol O} \times \text{molar mass O}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 = \frac{4 \times 16.00 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{64.00 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100$$

$$\% \text{ O} = 35.52 \%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

### Check Your Learning

To three significant digits, what is the mass percentage of iron in the compound  $\text{Fe}_2\text{O}_3$ ?

**Note:**

**Answer:**

69.9% Fe

## Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. This is accomplished using molar masses to convert the mass of each element to a number of moles. These molar amounts are used to compute whole-number ratios that can be used to derive the empirical formula of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

**Equation:**



$$1.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.142 \text{ mol C}$$

$$0.287 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.284 \text{ mol H}$$

Thus, this compound may be represented by the formula  $\text{C}_{0.142}\text{H}_{0.284}$ . Per convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

**Equation:**

$$\text{C} \frac{0.142}{0.142} \text{H} \frac{0.284}{0.142} \text{ or } \text{CH}_2$$

(Recall that subscripts of “1” are not written but rather assumed if no other number is present.)

The empirical formula for this compound is thus  $\text{CH}_2$ . This may or not be the compound’s *molecular formula* as well; however, additional information is needed to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

**Equation:**

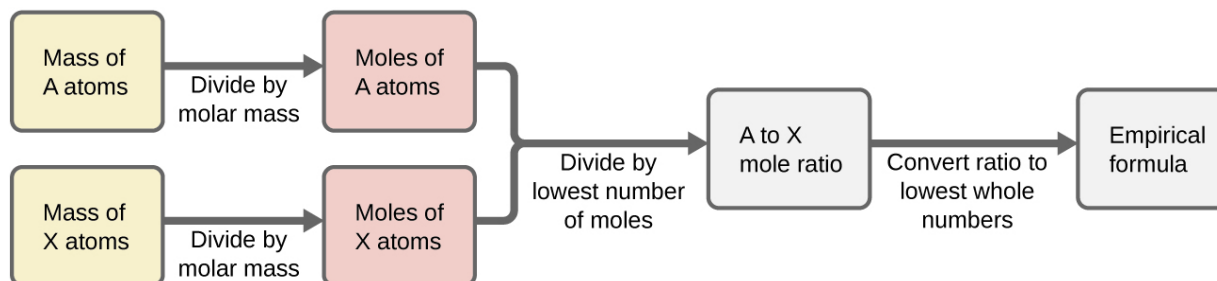
$$\text{Cl}_{0.150}\text{O}_{0.525} = \text{Cl} \frac{0.150}{0.150} \text{O} \frac{0.525}{0.150} = \text{ClO}_{3.5}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, multiply each of the subscripts by two, retaining the same atom ratio and yielding  $\text{Cl}_2\text{O}_7$  as the final empirical formula.

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element’s molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

[\[link\]](#) outlines this procedure in flow chart fashion for a substance containing elements A and X.



The empirical formula of a compound can be derived from the masses of all elements in the sample.

### Example:

#### Determining a Compound's Empirical Formula from the Masses of Its Elements

A sample of the black mineral hematite ([\[link\]](#)), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

**Solution**

This problem provides the mass in grams of each element. Begin by finding the moles of each:

**Equation:**

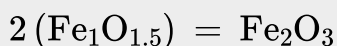
$$34.97 \text{ g Fe} \left( \frac{\text{mol Fe}}{55.85 \text{ g}} \right) = 0.6261 \text{ mol Fe}$$
$$15.03 \text{ g O} \left( \frac{\text{mol O}}{16.00 \text{ g}} \right) = 0.9394 \text{ mol O}$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

**Equation:**

$$\frac{0.6261}{0.6261} = 1.000 \text{ mol Fe}$$
$$\frac{0.9394}{0.6261} = 1.500 \text{ mol O}$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ( $\text{Fe}_1\text{O}_{1.5}$ ). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

**Equation:**

The empirical formula is  $\text{Fe}_2\text{O}_3$ .

**Check Your Learning**

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

**Note:****Answer:**

**Note:**

For additional worked examples illustrating the derivation of empirical formulas, watch the brief [video](#) clip.

**Deriving Empirical Formulas from Percent Composition**

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

**Example:****Determining an Empirical Formula from Percent Composition**

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O ([link](#)). What is the empirical formula for this gas?



An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

**Solution**

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the "percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

**Equation:**

$$\begin{aligned}
 27.29\% \text{ C} &= \frac{27.29 \text{ g C}}{100 \text{ g compound}} \\
 72.71\% \text{ O} &= \frac{72.71 \text{ g O}}{100 \text{ g compound}}
 \end{aligned}$$

The molar amounts of carbon and oxygen in a 100-g sample are calculated by dividing each element's mass by its molar mass:

**Equation:**

$$\begin{aligned}
 27.29 \text{ g C} \left( \frac{\text{mol C}}{12.01 \text{ g}} \right) &= 2.272 \text{ mol C} \\
 72.71 \text{ g O} \left( \frac{\text{mol O}}{16.00 \text{ g}} \right) &= 4.544 \text{ mol O}
 \end{aligned}$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

**Equation:**

$$\begin{aligned}
 \frac{2.272 \text{ mol C}}{2.272} &= 1 \\
 \frac{4.544 \text{ mol O}}{2.272} &= 2
 \end{aligned}$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is  $\text{CO}_2$ .

### Check Your Learning

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

**Note:**

**Answer:**



## Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in a previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its **empirical formula mass**. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If the molecular (or molar) mass of the substance is known, it may be divided by the empirical formula mass to yield the number of empirical formula units per molecule ( $n$ ):

**Equation:**

$$\frac{\text{molecular or molar mass (amu or } \frac{\text{g}}{\text{mol}} \text{)}}{\text{empirical formula mass (amu or } \frac{\text{g}}{\text{mol}} \text{)}} = n \text{ formula units/molecule}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by  $n$ , as shown by the generic empirical formula  $A_xB_y$ :

**Equation:**

$$(A_xB_y)_n = A_{nx}B_{ny}$$

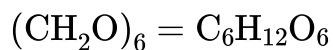
For example, consider a covalent compound whose empirical formula is determined to be  $\text{CH}_2\text{O}$ . The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

**Equation:**

$$\frac{180 \text{ amu/molecule}}{30 \frac{\text{amu}}{\text{formula unit}}} = 6 \text{ formula units/molecule}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

**Equation:**



Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, *one mole* of empirical formula units and molecules is considered, as opposed to single units and molecules.

**Example:**

**Determination of the Molecular Formula for Nicotine**

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

**Solution**

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

**Equation:**

$$(74.02 \text{ g C}) \left( \frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 6.163 \text{ mol C}$$

$$(8.710 \text{ g H}) \left( \frac{1 \text{ mol H}}{1.01 \text{ g H}} \right) = 8.624 \text{ mol H}$$

$$(17.27 \text{ g N}) \left( \frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 1.233 \text{ mol N}$$

Next, calculate the molar ratios of these elements relative to the least abundant element, N.

**Equation:**

$$6.163 \text{ mol C} / 1.233 \text{ mol N} = 5$$

**Equation:**

$$8.264 \text{ mol H} / 1.233 \text{ mol N} = 7$$



**Equation:**

$$1.233 \text{ mol N} / 1.233 \text{ mol N} = 1$$

**Equation:**

$$\begin{aligned}\frac{1.233}{1.233} &= 1.000 \text{ mol N} \\ \frac{6.163}{1.233} &= 4.998 \text{ mol C} \\ \frac{8.624}{1.233} &= 6.994 \text{ mol H}\end{aligned}$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is  $\text{C}_5\text{H}_7\text{N}$ . The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

Calculate the molar mass for nicotine from the given mass and molar amount of compound:

**Equation:**

$$\frac{40.57 \text{ g nicotine}}{0.2500 \text{ mol nicotine}} = \frac{162.3 \text{ g}}{\text{mol}}$$

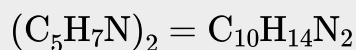
Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

**Equation:**

$$\frac{162.3 \text{ g/mol}}{81.13 \frac{\text{g}}{\text{formula unit}}} = 2 \text{ formula units/molecule}$$

Finally, derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

**Equation:**



### Check Your Learning

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

**Note:**

**Answer:**



## Key Concepts and Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

### Exercise:

#### Problem:

What information is needed to determine the molecular formula of a compound from the empirical formula?

### Exercise:

**Problem:** Calculate the following to four significant figures:

- (a) the percent composition of ammonia,  $\text{NH}_3$
- (b) the percent composition of photographic fixer solution "hypo,"  $\text{Na}_2\text{S}_2\text{O}_3$
- (c) the percent of calcium ion in  $\text{Ca}_3(\text{PO}_4)_2$

---

#### Solution:

- (a) % N = 82.24%  
% H = 17.76%;
- (b) % Na = 29.08%  
% S = 40.56%  
% O = 30.36%;
- (c) %  $\text{Ca}^{2+}$  = 38.76%

### Exercise:

**Problem:** Determine the following to four significant figures:

- (a) the percent composition of hydrazoic acid,  $\text{HN}_3$
- (b) the percent composition of TNT,  $\text{C}_6\text{H}_2(\text{CH}_3)(\text{NO}_2)_3$
- (c) the percent of  $\text{SO}_4^{2-}$  in  $\text{Al}_2(\text{SO}_4)_3$

**Exercise:**

**Problem:**

Determine the percent ammonia,  $\text{NH}_3$ , in  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ , to three significant figures.

---

**Solution:**

$$\% \text{NH}_3 = 38.2\%$$

**Exercise:**

**Problem:**

Determine the percent water in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to three significant figures.

**Exercise:**

**Problem:**

Determine the empirical formulas for compounds with the following percent compositions:

- (a) 15.8% carbon and 84.2% sulfur
  - (b) 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen
- 

**Solution:**

- (a)  $\text{CS}_2$
- (b)  $\text{CH}_2\text{O}$

**Exercise:**

**Problem:**

Determine the empirical formulas for compounds with the following percent compositions:

- (a) 43.6% phosphorus and 56.4% oxygen

(b) 28.7% K, 1.5% H, 22.8% P, and 47.0% O

**Exercise:**

**Problem:**

A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula?

---

**Solution:**



**Exercise:**

**Problem:**

Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3% carbon and 4.1% hydrogen. What is its molecular formula?

**Exercise:**

**Problem:**

Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol.

---

**Solution:**

$\text{Mg}_3\text{Si}_2\text{H}_3\text{O}_8$  (empirical formula),  $\text{Mg}_6\text{Si}_4\text{H}_6\text{O}_{16}$  (molecular formula)

**Exercise:**

**Problem:**

Polymers are large molecules composed of simple units repeated many times. Thus, they often have relatively simple empirical formulas. Calculate the empirical formulas of the following polymers:

(a) Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O

(b) Saran; 24.8% C, 2.0% H, 73.1% Cl

(c) polyethylene; 86% C, 14% H

(d) polystyrene; 92.3% C, 7.7% H

(e) Orlon; 67.9% C, 5.70% H, 26.4% N

### Exercise:

#### Problem:

A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95% C, 17.72% N, and 6.33% H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye.

---

#### Solution:



### Key Equations

$$\% \text{ X} = \frac{\text{mass X}}{\text{mass compound}} \times 100 \%$$

$$\frac{\text{molecular or molar mass (amu or } \frac{\text{g}}{\text{mol}})}{\text{empirical formula mass (amu or } \frac{\text{g}}{\text{mol}})} = n \text{ formula units/molecule}$$

$$(\text{A}_x\text{B}_y)_n = \text{A}_{nx}\text{B}_{ny}$$

### Glossary

empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

percent composition

percentage by mass of the various elements in a compound

## Molarity

By the end of this section, you will be able to:

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

Preceding sections of this chapter focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an “alloy”) determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see [\[link\]](#)). This section will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

## Solutions

Solutions have previously been defined as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. A more thorough treatment of solution properties is provided in the chapter on solutions and colloids, but provided here is an introduction to some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the **solvent** and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity (M)** is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

**Equation:**

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

### Example:

#### Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

#### Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

**Equation:**

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.375 M$$

### Check Your Learning

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

**Note:**

**Answer:**

0.05 M

### Example:

#### Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from [\[link\]](#)?

#### Solution

Rearrange the definition of molarity to isolate the quantity sought, moles of sugar, then substitute the value for molarity derived in [\[link\]](#), 0.375 M:

#### Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 0.375 \frac{\text{mol sugar}}{\text{L}} \times \left(10 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right) = 0.004 \text{ mol sugar}$$

### Check Your Learning

What volume (mL) of the sweetened tea described in [\[link\]](#) contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

**Note:**

**Answer:**

80 mL



**Example:****Calculating Molar Concentrations from the Mass of Solute**

Distilled white vinegar ([link](#)) is a solution of acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Distilled white vinegar is a solution of acetic acid in water.

**Solution**

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. Since the mass of solute is provided instead of its molar amount, use the solute's molar mass to obtain the amount of solute in moles:

**Equation:**

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2 \text{ g CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol CH}_3\text{CO}_2\text{H}}{60.052 \text{ g CH}_3\text{CO}_2\text{H}}}{0.500 \text{ L solution}} = 0.839 M$$

**Equation:**

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839 M$$

$$M = \frac{0.839 \text{ mol solute}}{1.00 \text{ L solution}}$$

### Check Your Learning

Calculate the molarity of 6.52 g of  $\text{CoCl}_2$  (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

**Note:**

**Answer:**

0.674 M

### Example:

#### Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-M solution?

#### Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in [\[link\]](#):

#### Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 5.30 \frac{\text{mol NaCl}}{\text{L}} \times 0.250 \text{ L} = 1.325 \text{ mol NaCl}$$

Finally, this molar amount is used to derive the mass of NaCl:

#### Equation:

$$1.325 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} = 77.4 \text{ g NaCl}$$

### Check Your Learning

How many grams of  $\text{CaCl}_2$  (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

**Note:**

**Answer:**

5.55 g CaCl<sub>2</sub>

When performing calculations stepwise, as in [\[link\]](#), it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In [\[link\]](#), the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If the guard digit had not been retained, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, rounding errors may also be avoided by performing computations in a single step (see [\[link\]](#)). This eliminates intermediate steps so that only the final result is rounded.

**Example:**

**Determining the Volume of Solution Containing a Given Mass of Solute**

In [\[link\]](#), the concentration of acetic acid in white vinegar was determined to be 0.839 M. What volume of vinegar contains 75.6 g of acetic acid?

**Solution**

First, use the molar mass to calculate moles of acetic acid from the given mass:

**Equation:**

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

**Equation:**

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

**Equation:**

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

**Equation:**

$$75.6 \text{ g CH}_3\text{CO}_2\text{H} \left( \frac{\text{mol CH}_3\text{CO}_2\text{H}}{60.05 \text{ g}} \right) \left( \frac{\text{L solution}}{0.839 \text{ mol CH}_3\text{CO}_2\text{H}} \right) = 1.50 \text{ L solution}$$

**Check Your Learning**

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

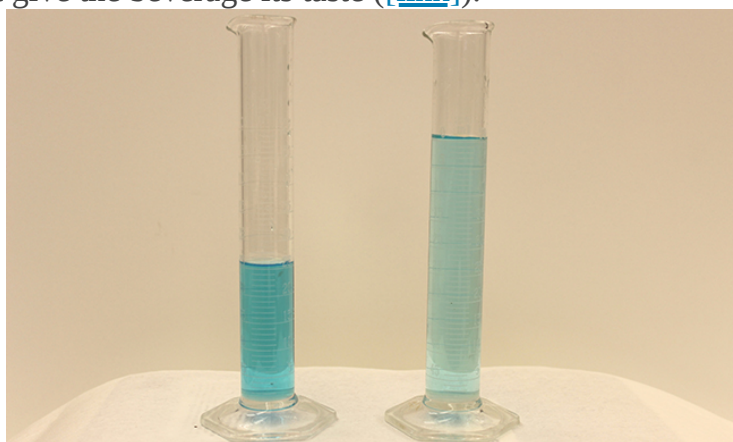
**Note:**

**Answer:**

0.370 L

## Dilution of Solutions

**Dilution** is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste ([link](#)).



Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute

because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, a solution of lesser concentration may be prepared. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents.

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the number of moles of solute in a solution ( $n$ ) is equal to the product of the solution's molarity ( $M$ ) and its volume in liters ( $L$ ):

**Equation:**

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

**Equation:**

$$n_1 = M_1L_1$$

**Equation:**

$$n_2 = M_2L_2$$

where the subscripts “1” and “2” refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution*,  $n_1 = n_2$ . Thus, these two equations may be set equal to one another:

**Equation:**

$$M_1L_1 = M_2L_2$$

This relation is commonly referred to as the dilution equation. Although this equation uses molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used as long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

**Equation:**

$$C_1V_1 = C_2V_2$$

where  $C$  and  $V$  are concentration and volume, respectively.

**Note:**

Use the [simulation](#) to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

**Example:**

**Determining the Concentration of a Diluted Solution**

If 0.850 L of a 5.00- $M$  solution of copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

**Solution**

The stock concentration,  $C_1$ , and volume,  $V_1$ , are provided as well as the volume of the diluted solution,  $V_2$ . Rearrange the dilution equation to isolate the unknown property, the concentration of the diluted solution,  $C_2$ :

**Equation:**

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), the diluted solution's concentration is expected to be less than one-half 5  $M$ . This ballpark estimate will be compared to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

**Equation:**

$$C_2 = \frac{0.850 \text{ L} \times 5.00 \frac{\text{mol}}{\text{L}}}{1.80 \text{ L}} = 2.36 \text{ M}$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5  $M$ ).

**Check Your Learning**

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04- $M$  solution of  $\text{CH}_3\text{OH}$  to 500.0 mL?

**Note:**

**Answer:**

0.102 M CH<sub>3</sub>OH

**Example:**

**Volume of a Diluted Solution**

What volume of 0.12 M HBr can be prepared from 11 mL (0.011 L) of 0.45 M HBr?

**Solution**

Provided are the volume and concentration of a stock solution,  $V_1$  and  $C_1$ , and the concentration of the resultant diluted solution,  $C_2$ . Find the volume of the diluted solution,  $V_2$  by rearranging the dilution equation to isolate  $V_2$ :

**Equation:**

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 M) is slightly more than one-fourth the original concentration (0.45 M), the volume of the diluted solution is expected to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

**Equation:**

$$V_2 = \frac{(0.45\text{ M})(0.011\text{ L})}{(0.12\text{ M})}$$

$$V_2 = 0.041\text{ L}$$

The volume of the 0.12-M solution is 0.041 L (41 mL). The result is reasonable and compares well with the rough estimate.

**Check Your Learning**

A laboratory experiment calls for 0.125 M HNO<sub>3</sub>. What volume of 0.125 M HNO<sub>3</sub> can be prepared from 0.250 L of 1.88 M HNO<sub>3</sub>?

**Note:**

**Answer:**

3.76 L

**Example:**

**Volume of a Concentrated Solution Needed for Dilution**

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

**Solution**

Given are the concentration of a stock solution,  $C_1$ , and the volume and concentration of the resultant diluted solution,  $V_2$  and  $C_2$ . Find the volume of the stock solution,  $V_1$  by rearranging the dilution equation to isolate  $V_1$ :

**Equation:**

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), the volume of the stock solution is expected to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

**Equation:**

$$V_1 = \frac{(0.100\text{ M})(5.00\text{ L})}{1.59\text{ M}}$$
$$V_1 = 0.314\text{ L}$$

Thus, 0.314 L of the 1.59-*M* solution is needed to prepare the desired solution. This result is consistent with the rough estimate.

**Check Your Learning**

What volume of a 0.575-*M* solution of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

**Note:**

**Answer:**

0.261 L



---

## Key Concepts and Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

### Exercise:

#### Problem:

What information is needed to calculate the molarity of a sulfuric acid solution?

---

#### Solution:

We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

### Exercise:

#### Problem:

A 200-mL sample and a 400-mL sample of a solution of salt have the same molarity. In what ways are the two samples identical? In what ways are these two samples different?

### Exercise:

**Problem:** Determine the molarity for each of the following solutions:

- (a) 0.444 mol of  $\text{CoCl}_2$  in 0.654 L of solution
  - (b) 98.0 g of phosphoric acid,  $\text{H}_3\text{PO}_4$ , in 1.00 L of solution
  - (c) 0.2074 g of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , in 40.00 mL of solution
  - (d) 10.5 kg of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in 18.60 L of solution
  - (e)  $7.0 \times 10^{-3}$  mol of  $\text{I}_2$  in 100.0 mL of solution
  - (f)  $1.8 \times 10^4$  mg of  $\text{HCl}$  in 0.075 L of solution
- 

**Solution:**

- (a) 0.679 M; (b) 1.00 M; (c) 0.06998 M; (d) 1.75 M; (e) 0.070 M; (f) 6.6 M

**Exercise:**

**Problem:** Determine the molarity of each of the following solutions:

- (a) 1.457 mol  $\text{KCl}$  in 1.500 L of solution
- (b) 0.515 g of  $\text{H}_2\text{SO}_4$  in 1.00 L of solution
- (c) 20.54 g of  $\text{Al}(\text{NO}_3)_3$  in 1575 mL of solution
- (d) 2.76 kg of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 1.45 L of solution
- (e) 0.005653 mol of  $\text{Br}_2$  in 10.00 mL of solution
- (f) 0.000889 g of glycine,  $\text{C}_2\text{H}_5\text{NO}_2$ , in 1.05 mL of solution

**Exercise:**

**Problem:**

Consider this question: What is the mass of the solute in 0.500 L of 0.30 M glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , used for intravenous injection?

- (a) Outline the steps necessary to answer the question.
  - (b) Answer the question.
- 

**Solution:**

- (a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles

and its molar mass; (b) 27 g

**Exercise:**

**Problem:**

Consider this question: What is the mass of solute in 200.0 L of a 1.556-*M* solution of KBr?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

**Exercise:**

**Problem:**

Calculate the number of moles and the mass of the solute in each of the following solutions:

- (a) 2.00 L of 18.5 *M* H<sub>2</sub>SO<sub>4</sub>, concentrated sulfuric acid
- (b) 100.0 mL of  $3.8 \times 10^{-6}$  *M* NaCN, the minimum lethal concentration of sodium cyanide in blood serum
- (c) 5.50 L of 13.3 *M* H<sub>2</sub>CO, the formaldehyde used to “fix” tissue samples
- (d) 325 mL of  $1.8 \times 10^{-6}$  *M* FeSO<sub>4</sub>, the minimum concentration of iron sulfate detectable by taste in drinking water

---

**Solution:**

(a) 37.0 mol H<sub>2</sub>SO<sub>4</sub>,  $3.63 \times 10^3$  g H<sub>2</sub>SO<sub>4</sub>; (b)  $3.8 \times 10^{-6}$  mol NaCN,  $1.9 \times 10^{-4}$  g NaCN; (c) 73.2 mol H<sub>2</sub>CO, 2.20 kg H<sub>2</sub>CO; (d)  $5.9 \times 10^{-7}$  mol FeSO<sub>4</sub>,  $8.9 \times 10^{-5}$  g FeSO<sub>4</sub>

**Exercise:**

**Problem:**

Calculate the number of moles and the mass of the solute in each of the following solutions:

- (a) 325 mL of  $8.23 \times 10^{-5}$  *M* KI, a source of iodine in the diet
- (b) 75.0 mL of  $2.2 \times 10^{-5}$  *M* H<sub>2</sub>SO<sub>4</sub>, a sample of acid rain
- (c) 0.2500 L of 0.1135 *M* K<sub>2</sub>CrO<sub>4</sub>, an analytical reagent used in iron assays

(d) 10.5 L of 3.716 M  $(\text{NH}_4)_2\text{SO}_4$ , a liquid fertilizer

**Exercise:**

**Problem:**

Consider this question: What is the molarity of  $\text{KMnO}_4$  in a solution of 0.0908 g of  $\text{KMnO}_4$  in 0.500 L of solution?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

---

**Solution:**

(a) Determine the molar mass of  $\text{KMnO}_4$ ; determine the number of moles of  $\text{KMnO}_4$  in the solution; from the number of moles and the volume of solution, determine the molarity; (b)  $1.15 \times 10^{-3} \text{ M}$

**Exercise:**

**Problem:**

Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

**Exercise:**

**Problem:** Calculate the molarity of each of the following solutions:

(a) 0.195 g of cholesterol,  $\text{C}_{27}\text{H}_{46}\text{O}$ , in 0.100 L of serum, the average concentration of cholesterol in human serum

(b) 4.25 g of  $\text{NH}_3$  in 0.500 L of solution, the concentration of  $\text{NH}_3$  in household ammonia

(c) 1.49 kg of isopropyl alcohol,  $\text{C}_3\text{H}_7\text{OH}$ , in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol

(d) 0.029 g of  $\text{I}_2$  in 0.100 L of solution, the solubility of  $\text{I}_2$  in water at 20 °C

---

**Solution:**

(a)  $5.04 \times 10^{-3} \text{ M}$ ; (b) 0.499 M; (c) 9.92 M; (d)  $1.1 \times 10^{-3} \text{ M}$

**Exercise:**

**Problem:** Calculate the molarity of each of the following solutions:

- (a) 293 g HCl in 666 mL of solution, a concentrated HCl solution
- (b) 2.026 g FeCl<sub>3</sub> in 0.1250 L of a solution used as an unknown in general chemistry laboratories
- (c) 0.001 mg Cd<sup>2+</sup> in 0.100 L, the maximum permissible concentration of cadmium in drinking water
- (d) 0.0079 g C<sub>7</sub>H<sub>5</sub>SNO<sub>3</sub> in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

**Exercise:**

**Problem:**

There is about 1.0 g of calcium, as Ca<sup>2+</sup>, in 1.0 L of milk. What is the molarity of Ca<sup>2+</sup> in milk?

---

**Solution:**

0.025 *M*

**Exercise:**

**Problem:**

What volume of a 1.00-*M* Fe(NO<sub>3</sub>)<sub>3</sub> solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 *M*?

**Exercise:**

**Problem:**

If 0.1718 L of a 0.3556-*M* C<sub>3</sub>H<sub>7</sub>OH solution is diluted to a concentration of 0.1222 *M*, what is the volume of the resulting solution?

---

**Solution:**

0.5000 L

**Exercise:**

**Problem:**

If 4.12 L of a 0.850 *M*-H<sub>3</sub>PO<sub>4</sub> solution is be diluted to a volume of 10.00 L, what is the concentration of the resulting solution?

**Exercise:****Problem:**

What volume of a 0.33-*M* C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 *M*?

---

**Solution:**

1.9 mL

**Exercise:****Problem:**

What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?

**Exercise:****Problem:**

What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

- (a) 1.00 L of a 0.250-*M* solution of Fe(NO<sub>3</sub>)<sub>3</sub> is diluted to a final volume of 2.00 L
  - (b) 0.5000 L of a 0.1222-*M* solution of C<sub>3</sub>H<sub>7</sub>OH is diluted to a final volume of 1.250 L
  - (c) 2.35 L of a 0.350-*M* solution of H<sub>3</sub>PO<sub>4</sub> is diluted to a final volume of 4.00 L
  - (d) 22.50 mL of a 0.025-*M* solution of C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> is diluted to 100.0 mL
- 

**Solution:**

(a) 0.125 *M*; (b) 0.04888 *M*; (c) 0.206 *M*; (d) 0.0056 *M*

**Exercise:**

**Problem:**

What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of  $\text{Na}_2\text{CO}_3$  is allowed to evaporate until the solution volume is reduced to 45.00 mL?

**Exercise:****Problem:**

A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

---

**Solution:**

11.9 *M*

**Exercise:****Problem:**

An experiment in a general chemistry laboratory calls for a 2.00-*M* solution of HCl. How many mL of 11.9 *M* HCl would be required to make 250 mL of 2.00 *M* HCl?

**Exercise:**

**Problem:** What volume of a 0.20-*M*  $\text{K}_2\text{SO}_4$  solution contains 57 g of  $\text{K}_2\text{SO}_4$ ?

---

**Solution:**

1.6 L

**Exercise:****Problem:**

The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), what is the maximum permissible molarity of that substance?

**Key Equations**

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$C_1V_1 = C_2V_2$$

## Glossary

aqueous solution

solution for which water is the solvent

concentrated

qualitative term for a solution containing solute at a relatively high concentration

concentration

quantitative measure of the relative amounts of solute and solvent present in a solution

dilute

qualitative term for a solution containing solute at a relatively low concentration

dilution

process of adding solvent to a solution in order to lower the concentration of solutes

dissolved

describes the process by which solute components are dispersed in a solvent

molarity ( $M$ )

unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute

solution component present in a concentration less than that of the solvent

solvent

solution component present in a concentration that is higher relative to other components



## Other Units for Solution Concentrations

By the end of this section, you will be able to:

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units

The previous section introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. This section will describe some other units of concentration that are commonly used in various applications, either for convenience or by convention.

## Mass Percentage

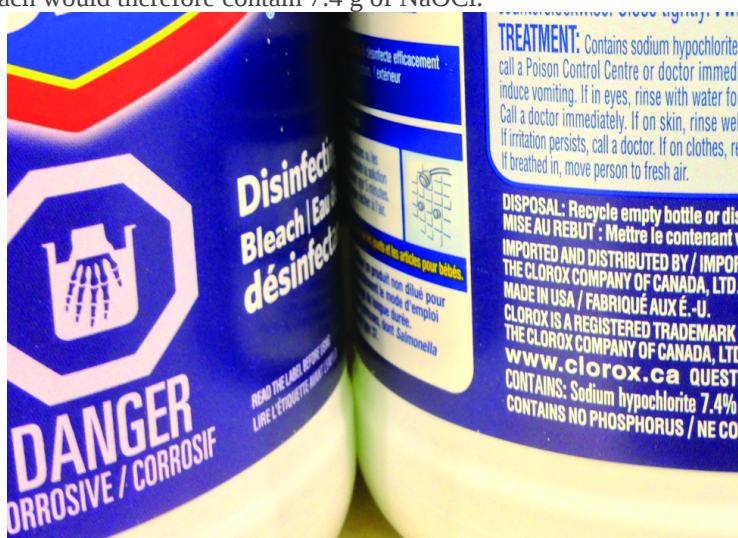
Earlier in this chapter, percent composition was introduced as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The **mass percentage** of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

**Equation:**

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\%$$

Mass percentage is also referred to by similar names such as *percent mass*, *percent weight*, *weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle ([link](#)) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.



Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

**Example:****Calculation of Percent by Mass**

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

**Solution**

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

**Equation:**

$$\% \text{ glucose} = \frac{3.75 \text{ mg glucose} \times \frac{1 \text{ g}}{1000 \text{ mg}}}{5.0 \text{ g spinal fluid}} = 0.075 \%$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, the solute mass unit in the numerator was converted from mg to g to match the units in the denominator. Alternatively, the spinal fluid mass unit in the denominator could have been converted from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

**Check Your Learning**

A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?

**Note:****Answer:**

14.8%

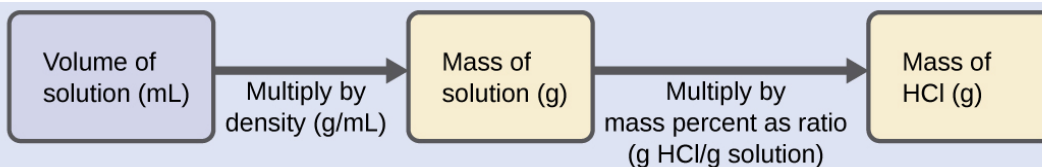
**Example:****Calculations using Mass Percentage**

“Concentrated” hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

**Solution**

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or  $5 \times 40 = 200$  g. In order to derive the mass of solute in a solution from its mass percentage, the mass of the solution must be known.

Using the solution density given, convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

**Equation:**

$$500 \text{ mL solution} \left( \frac{1.19 \text{ g solution}}{\text{mL solution}} \right) \left( \frac{37.2 \text{ g HCl}}{100 \text{ g solution}} \right) = 221 \text{ g HCl}$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

**Check Your Learning**

What volume of concentrated HCl solution contains 125 g of HCl?

**Note:**

**Answer:**

282 mL

## Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a **volume percentage**, %vol or (v/v)%:

**Equation:**

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

**Example:**

**Calculations using Volume Percentage**

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

**Solution**

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume.

Multiplying the isopropanol volume by its density yields the requested mass:

**Equation:**

$$(355 \text{ mL solution}) \left( \frac{70 \text{ mL isopropyl alcohol}}{100 \text{ mL solution}} \right) \left( \frac{0.785 \text{ g isopropyl alcohol}}{1 \text{ mL isopropyl alcohol}} \right) = 195 \text{ g isopropyl alcohol}$$

**Check Your Learning**

Wine is approximately 12% ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

**Note:**

**Answer:**

1.5 mol ethanol

## Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A **mass-volume percent** is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood ([link](#)).



(a)



(b)

“Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly)

## Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as **parts per million (ppm)** or **parts per billion (ppb)**. Like percentage (“part per hundred”) units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

**Equation:**

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm}$$
$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water ([link](#)).



(a)



(b)

(a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by “vastateparkstaff”/Wikimedia commons)

**Example:**

**Calculation of Parts per Million and Parts per Billion Concentrations**

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead ( $\mu\text{g}$ ) would be contained in a typical glass of water (300 mL)?

**Solution**

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb ( $1 \text{ ppm} = 10^3 \text{ ppb}$ ). Thus:

**Equation:**

$$15 \text{ ppb} \times \frac{1 \text{ ppm}}{10^3 \text{ ppb}} = 0.015 \text{ ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. Since the volume of solution (300 mL) is given, its density must be used to derive the corresponding mass. Assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

**Equation:**

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \frac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g}$$

Finally, convert this mass to the requested unit of micrograms:

**Equation:**

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \mu\text{g}$$

**Check Your Learning**

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

**Note:****Answer:**

9.6 ppm, 9600 ppb

**Section Summary**

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

**Exercise:****Problem:**

Consider this question: What mass of a concentrated solution of nitric acid (68.0%  $\text{HNO}_3$  by mass) is needed to prepare 400.0 g of a 10.0% solution of  $\text{HNO}_3$  by mass?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

---

**Solution:**

(a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units:  $\% \text{mass}_1 \times \text{mass}_1 = \% \text{mass}_2 \times \text{mass}_2$ . This equation can be rearranged to isolate  $\text{mass}_1$  and the given quantities substituted into this equation. (b) 58.8 g

**Exercise:**

**Problem:** What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

**Exercise:**

**Problem:**

What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.

---

**Solution:**

114 g

**Exercise:**

**Problem:**

What mass of HCl is contained in 45.0 mL of an aqueous HCl solution that has a density of  $1.19 \text{ g cm}^{-3}$  and contains 37.21% HCl by mass?

**Exercise:**

**Problem:**

The hardness of water (hardness count) is usually expressed in parts per million (by mass) of  $\text{CaCO}_3$ , which is equivalent to milligrams of  $\text{CaCO}_3$  per liter of water. What is the molar concentration of  $\text{Ca}^{2+}$  ions in a water sample with a hardness count of 175 mg  $\text{CaCO}_3/\text{L}$ ?

---

**Solution:**

$1.75 \times 10^{-3} \text{ M}$

**Exercise:**

**Problem:**

The level of mercury in a stream was suspected to be above the minimum considered safe (1 part per billion by weight). An analysis indicated that the concentration was 0.68 parts per billion. Assume a density of 1.0 g/mL and calculate the molarity of mercury in the stream.

**Exercise:**

**Problem:**

In Canada and the United Kingdom, devices that measure blood glucose levels provide a reading in millimoles per liter. If a measurement of 5.3 mM is observed, what is the concentration of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in mg/dL?

---

**Solution:**

95 mg/dL

**Exercise:**

**Problem:**

A throat spray is 1.40% by mass phenol,  $\text{C}_6\text{H}_5\text{OH}$ , in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.

**Exercise:**

**Problem:**

Copper(I) iodide ( $\text{CuI}$ ) is often added to table salt as a dietary source of iodine. How many moles of  $\text{CuI}$  are contained in 1.00 lb (454 g) of table salt containing 0.0100%  $\text{CuI}$  by mass?

---

**Solution:**

$2.38 \times 10^{-4} \text{ mol}$

**Exercise:**

**Problem:**

A cough syrup contains 5.0% ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , by mass. If the density of the solution is 0.9928 g/mL, determine the molarity of the alcohol in the cough syrup.

**Exercise:**

**Problem:**

D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.

---

**Solution:**

0.29 mol

**Exercise:**

**Problem:**

Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid,  $\text{H}_2\text{SO}_4$ , for which the density is 1.3057 g/mL.

## Key Equations

$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$
$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm}$
$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$

## Glossary



mass percentage

ratio of solute-to-solution mass expressed as a percentage

mass-volume percent

ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)

ratio of solute-to-solution mass multiplied by  $10^9$

parts per million (ppm)

ratio of solute-to-solution mass multiplied by  $10^6$

volume percentage

ratio of solute-to-solution volume expressed as a percentage

## Introduction

class="introduction"

- Writing and Balancing Chemical Equations
- Classifying Chemical Reactions
- Reaction Stoichiometry
- Reaction Yields
- Quantitative Chemical Analysis

Many  
modern  
rocket fuels  
are solid  
mixtures of  
substances  
combined in  
carefully  
measured  
amounts and  
ignited to  
yield a  
thrust-  
generating  
chemical  
reaction.  
(credit:  
modificatio  
n of work  
by NASA)



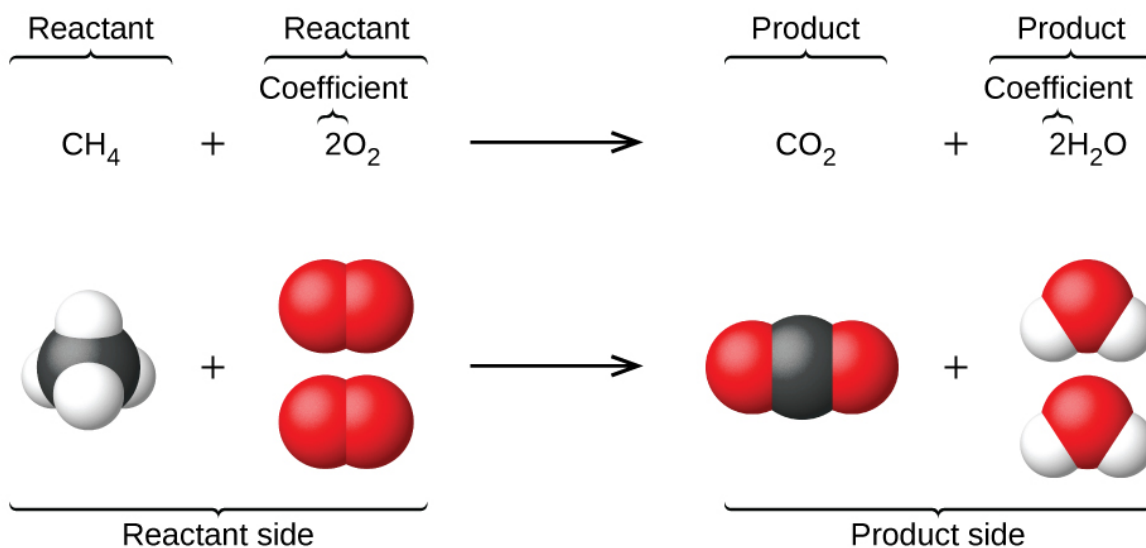
Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet ([\[link\]](#)). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

## Writing and Balancing Chemical Equations

By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

An earlier chapter of this text introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule ( $\text{CH}_4$ ) and two diatomic oxygen molecules ( $\text{O}_2$ ) to produce one carbon dioxide molecule ( $\text{CO}_2$ ) and two water molecules ( $\text{H}_2\text{O}$ ). The chemical equation representing this process is provided in the upper half of [\[link\]](#), with space-filling molecular models shown in the lower half of the figure.



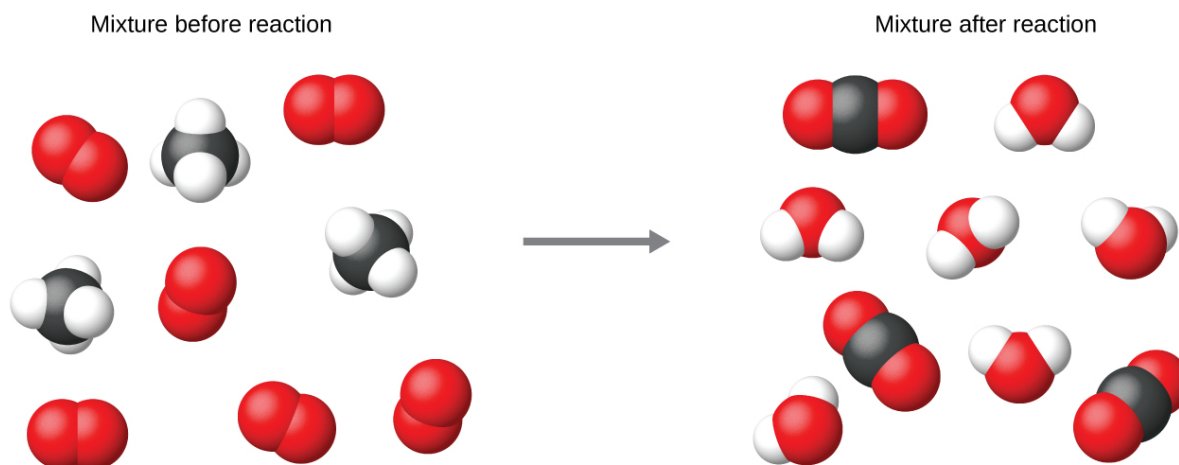
The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow ( $\longrightarrow$ ) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on ([\[link\]](#)). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- One methane molecule and two oxygen molecules react to yield one carbon dioxide molecule and two water molecules.
- One dozen methane molecules and two dozen oxygen molecules react to yield one dozen carbon dioxide molecules and two dozen water molecules.
- One mole of methane molecules and 2 moles of oxygen molecules react to yield 1 mole of carbon dioxide molecules and 2 moles of water molecules.



Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

## Balancing Equations

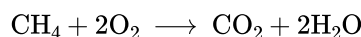
The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

**Equation:**

$$\left( 1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}} \right) + \left( 2 \text{ H}_2\text{O molecules} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}} \right) = 4 \text{ O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

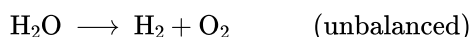
**Equation:**



Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	$1 = 1$ , yes
H	$4 \times 1 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	$4 = 4$ , yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

**Equation:**

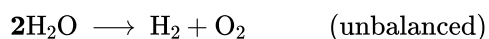


Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$ , no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{O}_2$  would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for  $\text{H}_2\text{O}$  to 2.

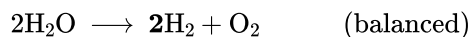
**Equation:**



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$ , no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the  $\text{H}_2$  product to 2.

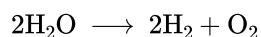
**Equation:**



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

**Equation:**



**Example:**

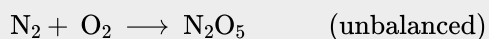
#### Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) to form dinitrogen pentoxide.

**Solution**

First, write the unbalanced equation.

**Equation:**



Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$ , yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	$2 \neq 5$ , no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the  $\text{O}_2$  and  $\text{N}_2\text{O}_5$  to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

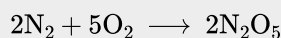
**Equation:**



Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$2 \times 2 = 4$	$2 \neq 4$ , no
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$ , yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant  $\text{N}_2$  to 2.

**Equation:**



Element	Reactants	Products	Balanced?
N	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$ , yes
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$ , yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

#### Check Your Learning

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

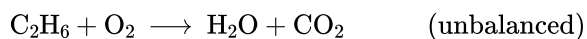
**Note:**

**Answer:**



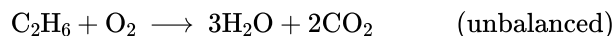
It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane ( $\text{C}_2\text{H}_6$ ) with oxygen to yield  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , represented by the unbalanced equation:

**Equation:**



Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

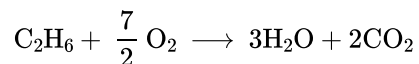
**Equation:**





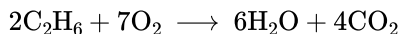
This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O<sub>2</sub> reactant to yield an odd number, so a fractional coefficient,  $\frac{7}{2}$ , is used instead to yield a provisional balanced equation:

**Equation:**



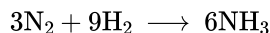
A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

**Equation:**



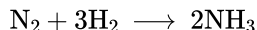
Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

**Equation:**



the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

**Equation:**



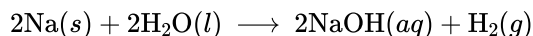
**Note:**

Use this interactive [tutorial](#) for additional practice balancing equations.

## Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

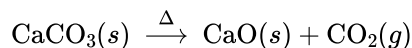
**Equation:**



This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta ( $\Delta$ ) over the arrow.

**Equation:**

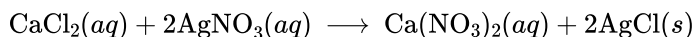


Other examples of these special conditions will be encountered in more depth in later chapters.

## Equations for Ionic Reactions

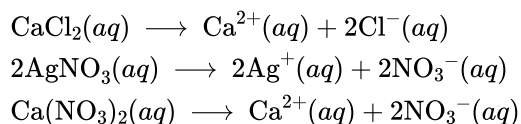
Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of  $\text{CaCl}_2$  and  $\text{AgNO}_3$  are mixed, a reaction takes place producing aqueous  $\text{Ca}(\text{NO}_3)_2$  and solid  $\text{AgCl}$ :

**Equation:**



This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogeneously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

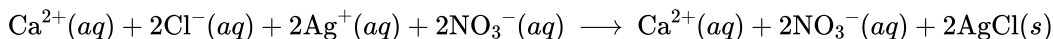
**Equation:**



Unlike these three ionic compounds,  $\text{AgCl}$  does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

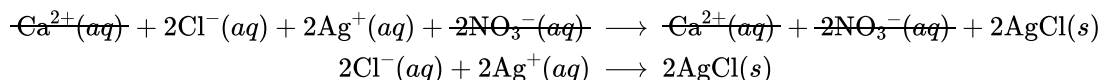
Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

**Equation:**



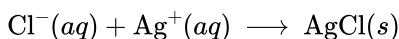
Examining this equation shows that two chemical species are present in identical form on both sides of the arrow,  $\text{Ca}^{2+}(aq)$  and  $\text{NO}_3^{-}(aq)$ . These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

**Equation:**



Following the convention of using the smallest possible integers as coefficients, this equation is then written:

**Equation:**



This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of  $\text{Cl}^-$  and  $\text{Ag}^+$ .

**Example:**

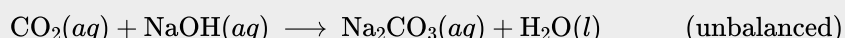
**Molecular and Ionic Equations**

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

**Solution**

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

**Equation:**



Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

**Equation:**



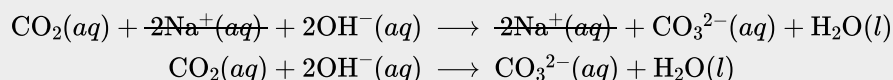
The two dissolved ionic compounds, NaOH and  $\text{Na}_2\text{CO}_3$ , can be represented as dissociated ions to yield the complete ionic equation:

**Equation:**



Finally, identify the spectator ion(s), in this case  $\text{Na}^+(aq)$ , and remove it from each side of the equation to generate the net ionic equation:

**Equation:**



**Check Your Learning**

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

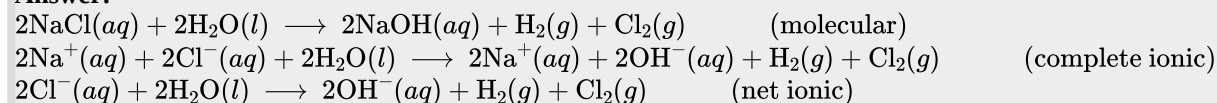
**Equation:**



Write balanced molecular, complete ionic, and net ionic equations for this process.

**Note:**

**Answer:**



## Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

---

#### Solution:

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

### Exercise:

**Problem:** Consider molecular, complete ionic, and net ionic equations.

- (a) What is the difference between these types of equations?
- (b) In what circumstance would the complete and net ionic equations for a reaction be identical?

### Exercise:

**Problem:** Balance the following equations:

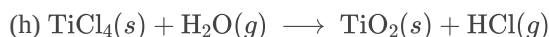
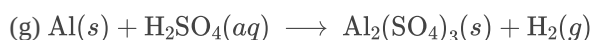
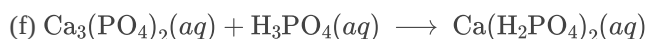
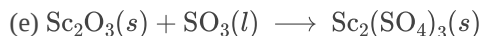
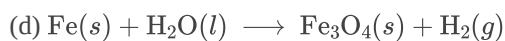
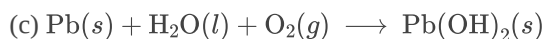
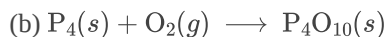
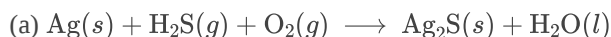
- (a)  $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + \text{HCl}(aq)$
  - (b)  $\text{Cu}(s) + \text{HNO}_3(aq) \longrightarrow \text{Cu}(\text{NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{NO}(g)$
  - (c)  $\text{H}_2(g) + \text{I}_2(s) \longrightarrow \text{HI}(s)$
  - (d)  $\text{Fe}(s) + \text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$
  - (e)  $\text{Na}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{NaOH}(aq) + \text{H}_2(g)$
  - (f)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + \text{H}_2\text{O}(g)$
  - (g)  $\text{P}_4(s) + \text{Cl}_2(g) \longrightarrow \text{PCl}_3(l)$
  - (h)  $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + \text{Cl}_2(g)$
- 

#### Solution:

- (a)  $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + 2\text{HCl}(aq)$ ; (b)  $3\text{Cu}(s) + 8\text{HNO}_3(aq) \longrightarrow 3\text{Cu}(\text{NO}_3)_2(aq) + 4\text{H}_2\text{O}(l) + 2\text{NO}(g)$ ; (c)  $\text{H}_2(g) + \text{I}_2(s) \longrightarrow 2\text{HI}(s)$ ; (d)  $4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$ ; (e)  $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$ ; (f)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + 4\text{H}_2\text{O}(g)$ ; (g)  $\text{P}_4(s) + 6\text{Cl}_2(g) \longrightarrow 4\text{PCl}_3(l)$ ; (h)  $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + 2\text{Cl}_2(g)$

**Exercise:**

**Problem:** Balance the following equations:

**Exercise:**

**Problem:** Write a balanced molecular equation describing each of the following chemical reactions.

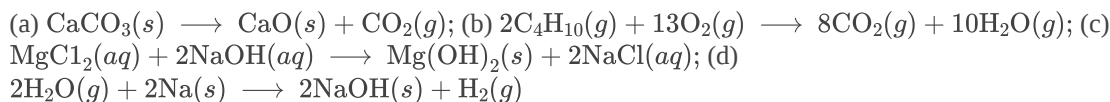
(a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.

(b) Gaseous butane,  $\text{C}_4\text{H}_{10}$ , reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.

(c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.

(d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

---

**Solution:****Exercise:**

**Problem:** Write a balanced equation describing each of the following chemical reactions.

(a) Solid potassium chlorate,  $\text{KClO}_3$ , decomposes to form solid potassium chloride and diatomic oxygen gas.

(b) Solid aluminum metal reacts with solid diatomic iodine to form solid  $\text{Al}_2\text{I}_6$ .

(c) When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.

(d) Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

**Exercise:****Problem:**

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

- (a) Write the formulas of barium nitrate and potassium chlorate.
- (b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
- (c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.
- (d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains  $\text{Fe}^{3+}$  ions.)

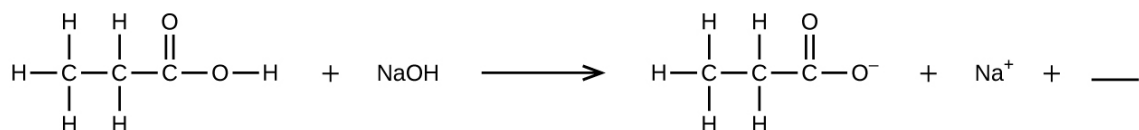
**Solution:**

(a)  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{KClO}_3$ ; (b)  $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$ ; (c)  $2\text{Ba}(\text{NO}_3)_2(s) \rightarrow 2\text{BaO}(s) + 2\text{N}_2(g) + 5\text{O}_2(g)$ ; (d)  $2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$ ;  $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$ ;  $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$

**Exercise:**

**Problem:**

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



**Exercise:**

**Problem:**

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

- (a) Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.
- (b) The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

**Solution:**

(a)  $4\text{HF}(aq) + \text{SiO}_2(s) \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O}(l)$ ; (b) complete ionic equation:  $2\text{Na}^+(aq) + 2\text{F}^-(aq) + \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{CaF}_2(s) + 2\text{Na}^+(aq) + 2\text{Cl}^-(aq)$ , net ionic equation:  $2\text{F}^-(aq) + \text{Ca}^{2+}(aq) \rightarrow \text{CaF}_2(s)$

**Exercise:**

**Problem:**

A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

- (a) The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

(b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

(c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

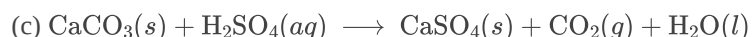
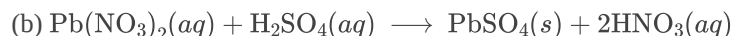
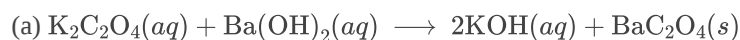
(d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

(e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

### Exercise:

#### Problem:

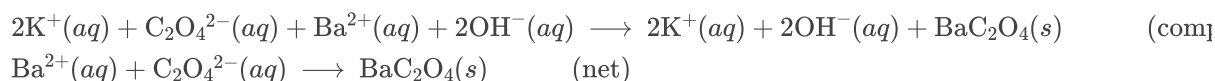
From the balanced molecular equations, write the complete ionic and net ionic equations for the following:



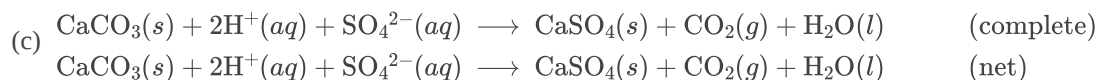
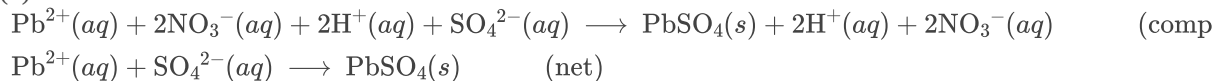
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#### Solution:

(a)



(b)



### Glossary

balanced equation

chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation

symbolic representation of a chemical reaction

coefficient

number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation

chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation

chemical equation in which all reactants and products are represented as neutral substances

net ionic equation

chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product

substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant

substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion

ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality



## Classifying Chemical Reactions

By the end of this section, you will be able to:

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

## Precipitation Reactions and Solubility Rules

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

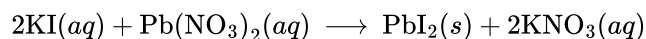
The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its **solubility**, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be **soluble**. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be **insoluble**, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in a later chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds ([link](#)).

Soluble Ionic Compounds	contain these ions	exceptions
	$\text{NH}_4^+$ group I cations: $\text{Li}^+$ $\text{Na}^+$ $\text{K}^+$ $\text{Rb}^+$	none

	Cs <sup>+</sup>	
	Cl <sup>-</sup> Br <sup>-</sup> I <sup>-</sup>	compounds with Ag <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup> , and Pb <sup>2+</sup>
	F <sup>-</sup>	compounds with group 2 metal cations, Pb <sup>2+</sup> and Fe <sup>3+</sup>
	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> HCO <sub>3</sub> <sup>-</sup> NO <sub>3</sub> <sup>-</sup> ClO <sub>3</sub> <sup>-</sup>	none
	SO <sub>4</sub> <sup>2-</sup>	compounds with Ag <sup>+</sup> , Ba <sup>2+</sup> , Ca <sup>2+</sup> , Hg <sub>2</sub> <sup>2+</sup> , Pb <sup>2+</sup> and Sr <sup>2+</sup>
<b>Insoluble Ionic Compounds</b>	contain these ions	exceptions
	CO <sub>3</sub> <sup>2-</sup> CrO <sub>4</sub> <sup>2-</sup> PO <sub>4</sub> <sup>3-</sup> S <sup>2-</sup>	compounds with group 1 cations and NH <sub>4</sub> <sup>+</sup>
	OH <sup>-</sup>	compounds with group 1 cations and Ba <sup>2+</sup>

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

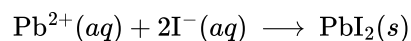
**Equation:**



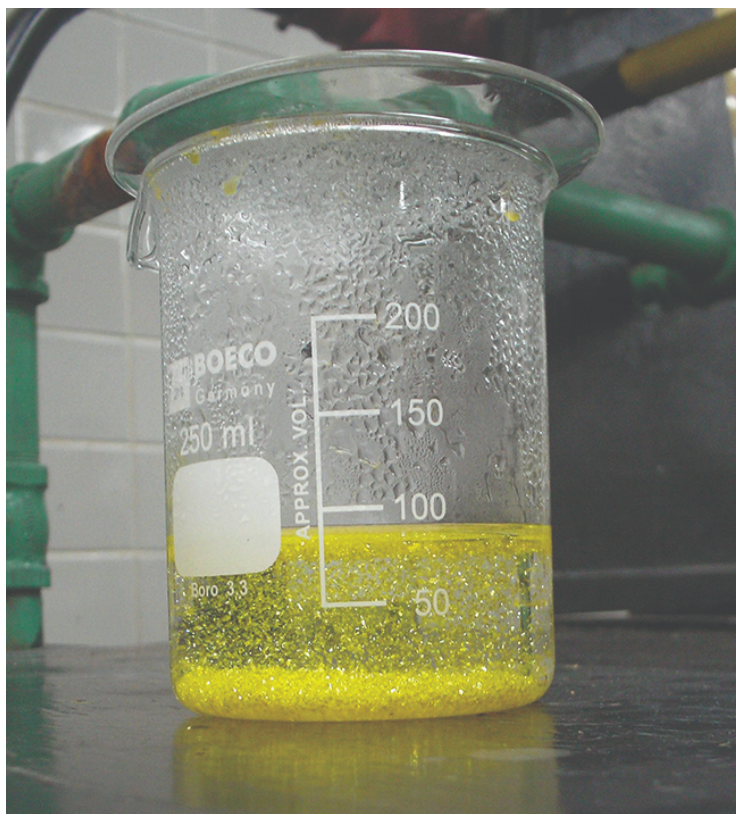
This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

**Equation:**



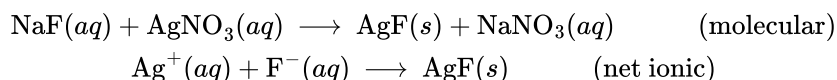
Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow ([link](#)). The properties of pure PbI<sub>2</sub> crystals make them useful for fabrication of X-ray and gamma ray detectors.



A precipitate of  $\text{PbI}_2$  forms when solutions containing  $\text{Pb}^{2+}$  and  $\text{I}^-$  are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in [\[link\]](#) may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing  $\text{Ag}^+$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ , and  $\text{F}^-$  ions. Aside from the two ionic compounds originally present in the solutions,  $\text{AgNO}_3$  and  $\text{NaF}$ , two additional ionic compounds may be derived from this collection of ions:  $\text{NaNO}_3$  and  $\text{AgF}$ . The solubility guidelines indicate all nitrate salts are soluble but that  $\text{AgF}$  is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

**Equation:**



### Example:

#### Predicting Precipitation Reactions

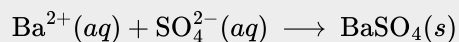
Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

- (a) potassium sulfate and barium nitrate
- (b) lithium chloride and silver acetate
- (c) lead nitrate and ammonium carbonate

**Solution**

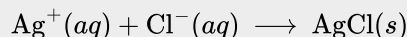
(a) The two possible products for this combination are  $\text{KNO}_3$  and  $\text{BaSO}_4$ . The solubility guidelines indicate  $\text{BaSO}_4$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

**Equation:**



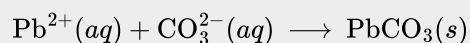
(b) The two possible products for this combination are  $\text{LiC}_2\text{H}_3\text{O}_2$  and  $\text{AgCl}$ . The solubility guidelines indicate  $\text{AgCl}$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

**Equation:**



(c) The two possible products for this combination are  $\text{PbCO}_3$  and  $\text{NH}_4\text{NO}_3$ . The solubility guidelines indicate  $\text{PbCO}_3$  is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

**Equation:**



### Check Your Learning

Which solution could be used to precipitate the barium ion,  $\text{Ba}^{2+}$ , in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

**Note:**

**Answer:**

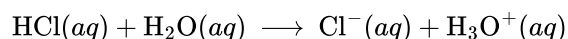
sodium sulfate,  $\text{BaSO}_4$

## Acid-Base Reactions

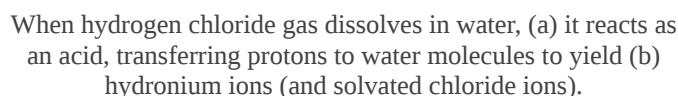
An **acid-base reaction** is one in which a hydrogen ion,  $\text{H}^+$ , is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions,  $\text{H}_3\text{O}^+$ . As an example, consider the equation shown here:

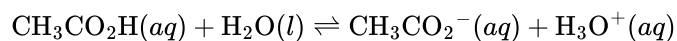
**Equation:**



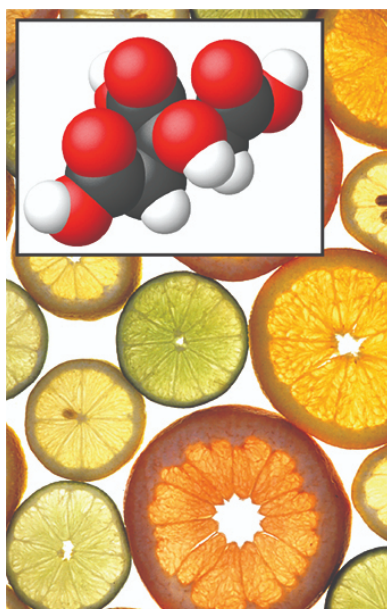
The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water,  $\text{H}_3\text{O}^+$  ions are produced by a chemical reaction in which  $\text{H}^+$  ions are transferred from  $\text{HCl}$  molecules to  $\text{H}_2\text{O}$  molecules ([link](#)).



**Equation:**



When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form,  $\text{CH}_3\text{CO}_2^-$  ([link](#)). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)



(a)



(b)

(a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

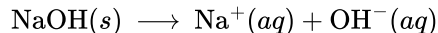
Common Strong Acids	
Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO <sub>3</sub>	nitric acid
HClO <sub>4</sub>	perchloric acid
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid

A **base** is a substance that will dissolve in water to yield hydroxide ions, OH<sup>-</sup>. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and Ca(OH)<sub>2</sub>. Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions directly into the solution. For

example, KOH and Ba(OH)<sub>2</sub> dissolve in water and dissociate completely to produce cations (K<sup>+</sup> and Ba<sup>2+</sup>, respectively) and hydroxide ions, OH<sup>-</sup>. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

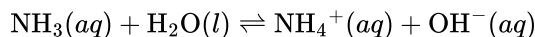
**Equation:**



This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na<sup>+</sup> and OH<sup>-</sup> ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners ([link](#)). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

**Equation:**



This is, by definition, an acid-base reaction, in this case involving the transfer of H<sup>+</sup> ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as NH<sub>4</sub><sup>+</sup> ions.



(a)



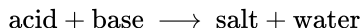
(b)

Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer.

(b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a **salt** and water

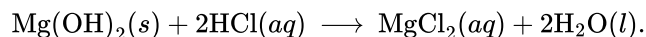
**Equation:**



To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid Mg(OH)<sub>2</sub>) is ingested to ease symptoms associated with excess stomach acid (HCl):

**Equation:**





Note that in addition to water, this reaction produces a salt, magnesium chloride.

**Example:**

**Writing Equations for Acid-Base Reactions**

Write balanced chemical equations for the acid-base reactions described here:

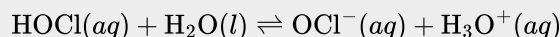
(a) the weak acid hydrogen hypochlorite reacts with water

(b) a solution of barium hydroxide is neutralized with a solution of nitric acid

**Solution**

(a) The two reactants are provided, HOCl and H<sub>2</sub>O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H<sup>+</sup> from HOCl to H<sub>2</sub>O to generate hydronium ions, H<sub>3</sub>O<sup>+</sup> and hypochlorite ions, OCl<sup>-</sup>.

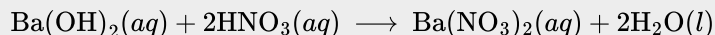
**Equation:**



A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, Ba(OH)<sub>2</sub> and HNO<sub>3</sub>. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba<sup>2+</sup>) and the anion generated when the acid transfers its hydrogen ion (NO<sub>3</sub><sup>-</sup>).

**Equation:**

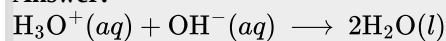


**Check Your Learning**

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

**Note:**

**Answer:**



**Note:**

**Stomach Antacids**

Our stomachs contain a solution of roughly 0.03 M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, CaCO<sub>3</sub>. The reaction,

**Equation:**

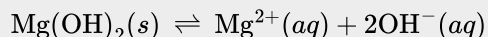


not only neutralizes stomach acid, it also produces CO<sub>2</sub>(g), which may result in a satisfying belch.



Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ . It works according to the reaction:

**Equation:**



The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

**Equation:**



This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

**Note:**

#### Culinary Aspects of Chemistry

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking.  $\text{NaHCO}_3$  is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish ([link](#)). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.



A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

**Note:**

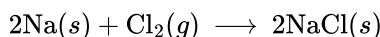
Explore the microscopic [view](#) of strong and weak acids and bases.

## Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen,  $O_2$ , a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving  $O_2$ , but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

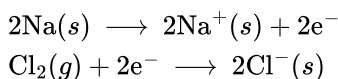
Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

**Equation:**



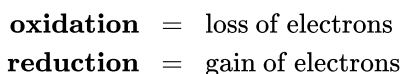
It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

**Equation:**



These equations show that Na atoms *lose electrons* while Cl atoms (in the  $Cl_2$  molecule) *gain electrons*, the “s” subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

**Equation:**



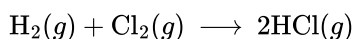
In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.

**Equation:**

**reducing agent** = species that is oxidized  
**oxidizing agent** = species that is reduced

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

**Equation:**



The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
  - Hydrogen: +1 when combined with nonmetals, -1 when combined with metals
  - Oxygen: -2 in most compounds, sometimes -1 (so-called peroxides,  $\text{O}_2^{2-}$ ), very rarely  $-\frac{1}{2}$  (so-called superoxides,  $\text{O}_2^-$ ), positive values when combined with F (values vary)
  - Halogens: -1 for F always, -1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

**Example:**

**Assigning Oxidation Numbers**

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

- (a)  $\text{H}_2\text{S}$
- (b)  $\text{SO}_3^{2-}$
- (c)  $\text{Na}_2\text{SO}_4$

**Solution**

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

**Equation:**

$$\begin{aligned}\text{charge on H}_2\text{S} = 0 &= (2 \times +1) + (1 \times x) \\ x &= 0 - (2 \times +1) = -2\end{aligned}$$

(b) Guideline 3 suggests the oxidation number for oxygen is -2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

**Equation:**

$$\begin{aligned}\text{charge on SO}_3^{2-} &= -2 = (3 \times -2) + (1 \times x) \\ x &= -2 - (3 \times -2) = +4\end{aligned}$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately. According to guideline 2, the oxidation number for sodium is +1. Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

**Equation:**

$$\begin{aligned}\text{charge on SO}_4^{2-} &= -2 = (4 \times -2) + (1 \times x) \\ x &= -2 - (4 \times -2) = +6\end{aligned}$$

### Check Your Learning

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

- (a) KNO<sub>3</sub>
- (b) AlH<sub>3</sub>
- (c) NH<sub>4</sub><sup>+</sup>
- (d) H<sub>2</sub>PO<sub>4</sub><sup>−</sup>

**Note:**

**Answer:**

(a) N, +5; (b) Al, +3; (c) N, −3; (d) P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist [\[link\]](#).) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

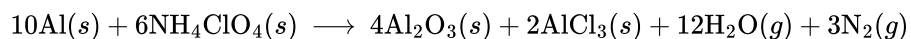
**Equation:**

$$\begin{aligned}\text{oxidation} &= \text{increase in oxidation number} \\ \text{reduction} &= \text{decrease in oxidation number}\end{aligned}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl<sub>2</sub> to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H<sub>2</sub> to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl<sub>2</sub> to −1 in HCl).

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted in [\[link\]](#) are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

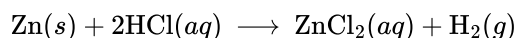
**Equation:**



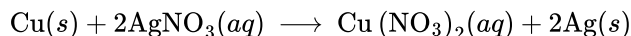
**Note:**

Watch a brief [video](#) showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

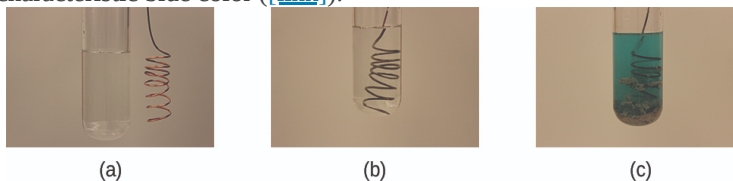
**Single-displacement (replacement) reactions** are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

**Equation:**

Metallic elements may also be oxidized by solutions of other metal salts; for example:

**Equation:**

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting  $\text{Cu}^{2+}$  ions dissolve in the solution to yield a characteristic blue color ([link](#)).



(a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

**Example:****Describing Redox Reactions**

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

- (a)  $\text{ZnCO}_3(s) \longrightarrow \text{ZnO}(s) + \text{CO}_2(g)$
- (b)  $2\text{Ga}(l) + 3\text{Br}_2(l) \longrightarrow 2\text{GaBr}_3(s)$
- (c)  $2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
- (d)  $\text{BaCl}_2(aq) + \text{K}_2\text{SO}_4(aq) \longrightarrow \text{BaSO}_4(s) + 2\text{KCl}(aq)$
- (e)  $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

**Solution**

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

(a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in  $\text{Ga}(l)$  to +3 in  $\text{GaBr}_3(s)$ . The reducing agent is  $\text{Ga}(l)$ . Bromine is reduced, its oxidation number decreasing from 0 in  $\text{Br}_2(l)$  to -1

in  $\text{GaBr}_3(\text{s})$ . The oxidizing agent is  $\text{Br}_2(\text{l})$ .

(c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction*). Oxygen is oxidized, its oxidation number increasing from  $-1$  in  $\text{H}_2\text{O}_2(\text{aq})$  to  $0$  in  $\text{O}_2(\text{g})$ . Oxygen is also reduced, its oxidation number decreasing from  $-1$  in  $\text{H}_2\text{O}_2(\text{aq})$  to  $-2$  in  $\text{H}_2\text{O}(\text{l})$ . For disproportionation reactions, the same substance functions as an oxidant and a reductant.

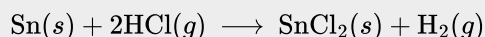
(d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from  $-2$  in  $\text{C}_2\text{H}_4(\text{g})$  to  $+4$  in  $\text{CO}_2(\text{g})$ . The reducing agent (fuel) is  $\text{C}_2\text{H}_4(\text{g})$ . Oxygen is reduced, its oxidation number decreasing from  $0$  in  $\text{O}_2(\text{g})$  to  $-2$  in  $\text{H}_2\text{O}(\text{l})$ . The oxidizing agent is  $\text{O}_2(\text{g})$ .

### Check Your Learning

This equation describes the production of tin(II) chloride:

**Equation:**



Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

**Note:**

**Answer:**

Yes, a single-replacement reaction.  $\text{Sn}(\text{s})$  is the reductant,  $\text{HCl}(\text{g})$  is the oxidant.

## Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding  $\text{H}_2\text{O}$  molecules.
4. Balance hydrogen atoms by adding  $\text{H}^+$  ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
  - a. Add  $\text{OH}^-$  ions to both sides of the equation in numbers equal to the number of  $\text{H}^+$  ions.
  - b. On the side of the equation containing both  $\text{H}^+$  and  $\text{OH}^-$  ions, combine these ions to yield water molecules.

c. Simplify the equation by removing any redundant water molecules.

9. Finally, check to see that both the number of atoms and the total charges<sup>[footnote]</sup> are balanced.

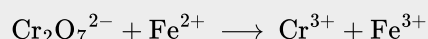
The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

### Example:

#### Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

#### Equation:



#### Solution

*Write the two half-reactions.* Each half-reaction will contain one reactant and one product with one element in common.

#### Equation:

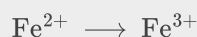


#### Equation:



*Balance all elements except oxygen and hydrogen.* The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

#### Equation:

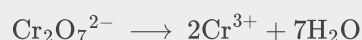


#### Equation:



*Balance oxygen atoms by adding H<sub>2</sub>O molecules.* The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

#### Equation:



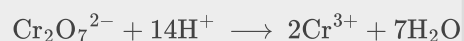
*Balance hydrogen atoms by adding H<sup>+</sup> ions.*

The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

#### Equation:



#### Equation:



*Balance charge by adding electrons.*

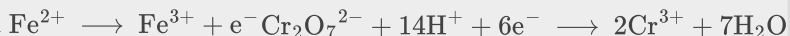
The chromium half-reaction shows a total charge of  $(1 \times 2-) + (14 \times 1+) = 12+$  on the left side and a total charge of  $2 \times 3+ = 6+$  on the right side.

(1  $\text{Cr}_2\text{O}_7^{2-}$  ion and 14  $\text{H}^+$  ions). The total charge on the right side (1  $\text{Fe}^{3+}$  ion). Adding one electron to the right side brings that side's total charge to  $(3+) + (1-) = 2+$ , and

#### Equation:



#### Equation:



charge balance is = 6+, and charge achieved.

balance is achieved.

**Equation:**

**Equation:**

Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

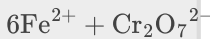
**Equation:**

Add the balanced half-reactions and cancel species that appear on both sides of the equation.



Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

**Equation:**



A final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

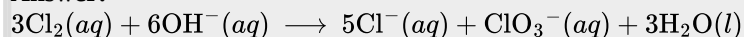
### Check Your Learning

In basic solution, molecular chlorine,  $\text{Cl}_2$ , reacts with hydroxide ions,  $\text{OH}^-$ , to yield chloride ions,  $\text{Cl}^-$ , and chlorate ions,  $\text{ClO}_3^-$ . HINT: This is a *disproportionation reaction* in which the element chlorine is both oxidized and reduced. Write a balanced equation for this reaction.



**Note:**

**Answer:**



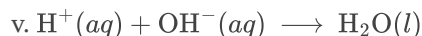
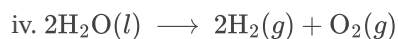
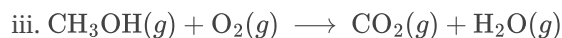
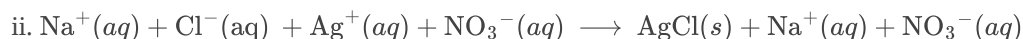
## Key Concepts and Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:** Use the following equations to answer the next four questions:



(a) Which equation describes a physical change?

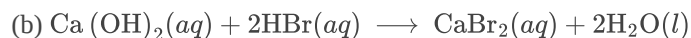
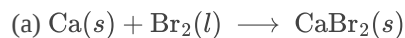
(b) Which equation identifies the reactants and products of a combustion reaction?

(c) Which equation is not balanced?

(d) Which is a net ionic equation?

**Exercise:**

**Problem:** Indicate what type, or types, of reaction each of the following represents:



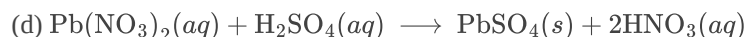
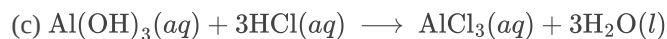
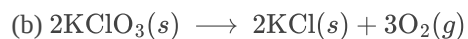
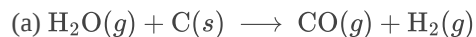
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**Solution:**

(a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

**Exercise:**

**Problem:** Indicate what type, or types, of reaction each of the following represents:



**Exercise:**

**Problem:**

Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction? Explain your answer.

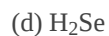
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**Solution:**

It is an oxidation-reduction reaction because the oxidation state of the silver changes during the reaction.

**Exercise:**

**Problem:** Determine the oxidation states of the elements in the following compounds:



**Exercise:**

**Problem:**

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.



**Solution:**

(a) H +1, P +5, O -2; (b) Al +3, H +1, O -2; (c) Se +4, O -2; (d) K +1, N +3, O -2; (e) In +3, S -2; (f) P +3, O -2

**Exercise:**

**Problem:**

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a)  $\text{H}_2\text{SO}_4$

(b)  $\text{Ca}(\text{OH})_2$

(c)  $\text{BrOH}$

(d)  $\text{ClNO}_2$

(e)  $\text{TiCl}_4$

(f)  $\text{NaH}$

**Exercise:**

**Problem:** Classify the following as acid-base reactions or oxidation-reduction reactions:

(a)  $\text{Na}_2\text{S}(aq) + 2\text{HCl}(aq) \longrightarrow 2\text{NaCl}(aq) + \text{H}_2\text{S}(g)$

(b)  $2\text{Na}(s) + 2\text{HCl}(aq) \longrightarrow 2\text{NaCl}(aq) + \text{H}_2(g)$

(c)  $\text{Mg}(s) + \text{Cl}_2(g) \longrightarrow \text{MgCl}_2(s)$

(d)  $\text{MgO}(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l)$

(e)  $\text{K}_3\text{P}(s) + 2\text{O}_2(g) \longrightarrow \text{K}_3\text{PO}_4(s)$

(f)  $3\text{KOH}(aq) + \text{H}_3\text{PO}_4(aq) \longrightarrow \text{K}_3\text{PO}_4(aq) + 3\text{H}_2\text{O}(l)$

---

**Solution:**

(a) acid-base; (b) oxidation-reduction: Na is oxidized,  $\text{H}^+$  is reduced; (c) oxidation-reduction: Mg is oxidized,  $\text{Cl}_2$  is reduced; (d) acid-base; (e) oxidation-reduction:  $\text{P}^{3-}$  is oxidized,  $\text{O}_2$  is reduced; (f) acid-base

**Exercise:**

**Problem:**

Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

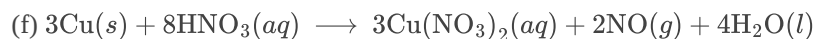
(a)  $\text{Mg}(s) + \text{NiCl}_2(aq) \longrightarrow \text{MgCl}_2(aq) + \text{Ni}(s)$

(b)  $\text{PCl}_3(l) + \text{Cl}_2(g) \longrightarrow \text{PCl}_5(s)$

(c)  $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$

(d)  $\text{Zn}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{ZnSO}_4(aq) + \text{H}_2(g)$

(e)  $2\text{K}_2\text{S}_2\text{O}_3(s) + \text{I}_2(s) \longrightarrow \text{K}_2\text{S}_4\text{O}_6(s) + 2\text{KI}(s)$

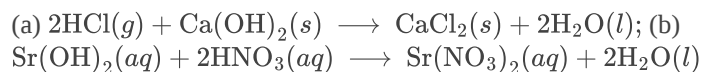


**Exercise:**

**Problem:** Complete and balance the following acid-base equations:



**Solution:**



**Exercise:**

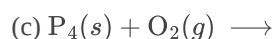
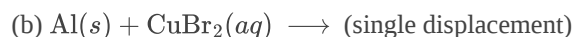
**Problem:** Complete and balance the following acid-base equations:



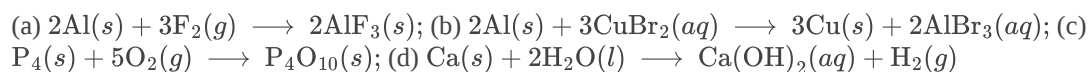
**Exercise:**

**Problem:**

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.



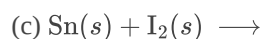
**Solution:**



**Exercise:**

**Problem:**

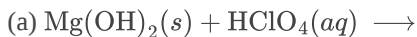
Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.



**Exercise:**

**Problem:**

Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.

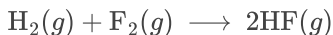
**Solution:****Exercise:****Problem:**

When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.

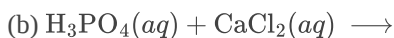
**Exercise:****Problem:**

The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

---

**Solution:****Exercise:**

**Problem:** Write the molecular, total ionic, and net ionic equations for the following reactions:

**Exercise:****Problem:**

Great Lakes Chemical Company produces bromine,  $\text{Br}_2$ , from bromide salts such as  $\text{NaBr}$ , in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of  $\text{NaBr}$  with  $\text{Cl}_2$ .

---

**Solution:****Exercise:**

**Problem:**

In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce MgO. MgO is a white solid, but in these experiments it often looks gray, due to small amounts of  $\text{Mg}_3\text{N}_2$ , a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.

**Exercise:****Problem:**

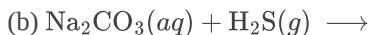
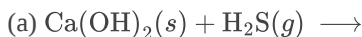
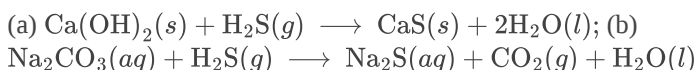
Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of  $\text{CO}_2$ . (Hint: Water is one of the products.)

**Solution:****Exercise:****Problem:**

Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate,  $\text{CaCO}_3$ , with propionic acid,  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ , which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.

**Exercise:****Problem:**

Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:

**Solution:****Exercise:****Problem:**

Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid hydrogen sulfate as the only product. Write the two equations which represent these reactions.

**Exercise:****Problem:**

Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.

(a) solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)

(b) gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction

(c) gaseous  $\text{H}_2\text{S}$  from solid  $\text{Zn}$  and  $\text{S}$  via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)

---

**Solution:**

(a) step 1:  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$ , step 2:  
 $\text{NH}_3(g) + \text{HNO}_3(aq) \longrightarrow \text{NH}_4\text{NO}_3(aq) \longrightarrow \text{NH}_4\text{NO}_3(s)$  (after drying); (b)  
 $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$ ; (c)  $\text{Zn}(s) + \text{S}(s) \longrightarrow \text{ZnS}(s)$  and  
 $\text{ZnS}(s) + 2\text{HCl}(aq) \longrightarrow \text{ZnCl}_2(aq) + \text{H}_2\text{S}(g)$

**Exercise:**

**Problem:**

Calcium cyclamate  $\text{Ca}(\text{C}_6\text{H}_{11}\text{NHSO}_3)_2$  is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid  $\text{C}_6\text{H}_{11}\text{NHSO}_3\text{H}$  with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.

**Exercise:**

**Problem:** Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

- (a)  $\text{Sn}^{4+}(aq) \longrightarrow \text{Sn}^{2+}(aq)$
  - (b)  $[\text{Ag}(\text{NH}_3)_2]^+(aq) \longrightarrow \text{Ag}(s) + \text{NH}_3(aq)$
  - (c)  $\text{Hg}_2\text{Cl}_2(s) \longrightarrow \text{Hg}(l) + \text{Cl}^-(aq)$
  - (d)  $\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g)$  (in acidic solution)
  - (e)  $\text{IO}_3^-(aq) \longrightarrow \text{I}_2(s)$  (in basic solution)
  - (f)  $\text{SO}_3^{2-}(aq) \longrightarrow \text{SO}_4^{2-}(aq)$  (in acidic solution)
  - (g)  $\text{MnO}_4^-(aq) \longrightarrow \text{Mn}^{2+}(aq)$  (in acidic solution)
  - (h)  $\text{Cl}^-(aq) \longrightarrow \text{ClO}_3^-(aq)$  (in basic solution)
- 

**Solution:**

(a)  $\text{Sn}^{4+}(aq) + 2e^- \longrightarrow \text{Sn}^{2+}(aq)$ , (b)  $[\text{Ag}(\text{NH}_3)_2]^+(aq) + e^- \longrightarrow \text{Ag}(s) + 2\text{NH}_3(aq)$ ; (c)  
 $\text{Hg}_2\text{Cl}_2(s) + 2e^- \longrightarrow 2\text{Hg}(l) + 2\text{Cl}^-(aq)$ ; (d)  $2\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$ ; (e)  
 $6\text{H}_2\text{O}(l) + 2\text{IO}_3^-(aq) + 10e^- \longrightarrow \text{I}_2(s) + 12\text{OH}^-(aq)$ ; (f)  
 $\text{H}_2\text{O}(l) + \text{SO}_3^{2-}(aq) \longrightarrow \text{SO}_4^{2-}(aq) + 2\text{H}^+(aq) + 2e^-$ ; (g)  
 $8\text{H}^+(aq) + \text{MnO}_4^-(aq) + 5e^- \longrightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$ ; (h)  
 $\text{Cl}^-(aq) + 6\text{OH}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + 3\text{H}_2\text{O}(l) + 6e^-$

**Exercise:**

**Problem:** Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

- (a)  $\text{Cr}^{2+}(aq) \longrightarrow \text{Cr}^{3+}(aq)$
- (b)  $\text{Hg}(l) + \text{Br}^-(aq) \longrightarrow \text{HgBr}_4^{2-}(aq)$
- (c)  $\text{ZnS}(s) \longrightarrow \text{Zn}(s) + \text{S}^{2-}(aq)$

- (d)  $\text{H}_2(g) \longrightarrow \text{H}_2\text{O}(l)$  (in basic solution)
- (e)  $\text{H}_2(g) \longrightarrow \text{H}_3\text{O}^+(aq)$  (in acidic solution)
- (f)  $\text{NO}_3^-(aq) \longrightarrow \text{HNO}_2(aq)$  (in acidic solution)
- (g)  $\text{MnO}_2(s) \longrightarrow \text{MnO}_4^-(aq)$  (in basic solution)
- (h)  $\text{Cl}^-(aq) \longrightarrow \text{ClO}_3^-(aq)$  (in acidic solution)

**Exercise:**

**Problem:** Balance each of the following equations according to the half-reaction method:

- (a)  $\text{Sn}^{2+}(aq) + \text{Cu}^{2+}(aq) \longrightarrow \text{Sn}^{4+}(aq) + \text{Cu}^+(aq)$
- (b)  $\text{H}_2\text{S}(g) + \text{Hg}_2^{2+}(aq) \longrightarrow \text{Hg}(l) + \text{S}(s)$  (in acid)
- (c)  $\text{CN}^-(aq) + \text{ClO}_2(aq) \longrightarrow \text{CNO}^-(aq) + \text{Cl}^-(aq)$  (in acid)
- (d)  $\text{Fe}^{2+}(aq) + \text{Ce}^{4+}(aq) \longrightarrow \text{Fe}^{3+}(aq) + \text{Ce}^{3+}(aq)$
- (e)  $\text{HBrO}(aq) \longrightarrow \text{Br}^-(aq) + \text{O}_2(g)$  (in acid)

**Solution:**

(a)  $\text{Sn}^{2+}(aq) + 2\text{Cu}^{2+}(aq) \longrightarrow \text{Sn}^{4+}(aq) + 2\text{Cu}^+(aq)$ ; (b)  $\text{H}_2\text{S}(g) + \text{Hg}_2^{2+}(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{Hg}(l) + \text{S}(s) + 2\text{H}_3\text{O}^+(aq)$ ; (c)  $5\text{CN}^-(aq) + 2\text{ClO}_2(aq) + 3\text{H}_2\text{O}(l) \longrightarrow 5\text{CNO}^-(aq) + 2\text{Cl}^-(aq) + 2\text{H}_3\text{O}^+(aq)$ ; (d)  $\text{Fe}^{2+}(aq) + \text{Ce}^{4+}(aq) \longrightarrow \text{Fe}^{3+}(aq) + \text{Ce}^{3+}(aq)$ ; (e)  $2\text{HBrO}(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{H}_3\text{O}^+(aq) + 2\text{Br}^-(aq) + \text{O}_2(g)$

**Exercise:**

**Problem:** Balance each of the following equations according to the half-reaction method:

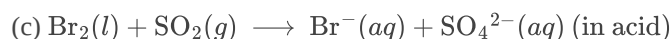
- (a)  $\text{Zn}(s) + \text{NO}_3^-(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{N}_2(g)$  (in acid)
- (b)  $\text{Zn}(s) + \text{NO}_3^-(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{NH}_3(aq)$  (in base)
- (c)  $\text{CuS}(s) + \text{NO}_3^-(aq) \longrightarrow \text{Cu}^{2+}(aq) + \text{S}(s) + \text{NO}(g)$  (in acid)
- (d)  $\text{NH}_3(aq) + \text{O}_2(g) \longrightarrow \text{NO}_2(g)$  (gas phase)
- (e)  $\text{H}_2\text{O}_2(aq) + \text{MnO}_4^-(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{O}_2(g)$  (in acid)
- (f)  $\text{NO}_2(g) \longrightarrow \text{NO}_3^-(aq) + \text{NO}_2^-(aq)$  (in base)
- (g)  $\text{Fe}^{3+}(aq) + \text{I}^-(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{I}_2(aq)$

**Exercise:**

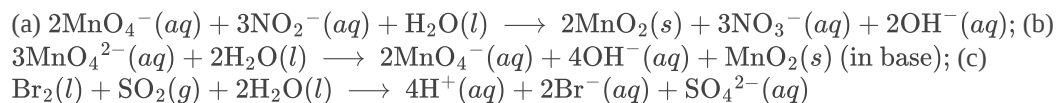
**Problem:** Balance each of the following equations according to the half-reaction method:

- (a)  $\text{MnO}_4^-(aq) + \text{NO}_2^-(aq) \longrightarrow \text{MnO}_2(s) + \text{NO}_3^-(aq)$  (in base)
- (b)  $\text{MnO}_4^{2-}(aq) \longrightarrow \text{MnO}_4^-(aq) + \text{MnO}_2(s)$  (in base)





**Solution:**



## Glossary

### acid

substance that produces  $\text{H}_3\text{O}^+$  when dissolved in water

### acid-base reaction

reaction involving the transfer of a hydrogen ion between reactant species

### base

substance that produces  $\text{OH}^-$  when dissolved in water

### combustion reaction

vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

### half-reaction

an equation that shows whether each reactant loses or gains electrons in a reaction.

### insoluble

of relatively low solubility; dissolving only to a slight extent

### neutralization reaction

reaction between an acid and a base to produce salt and water

### oxidation

process in which an element's oxidation number is increased by loss of electrons

### oxidation-reduction reaction

(also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

### oxidation number

(also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

### oxidizing agent

(also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

### precipitate

insoluble product that forms from reaction of soluble reactants

### precipitation reaction

reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

### reduction

process in which an element's oxidation number is decreased by gain of electrons

### reducing agent

(also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

salt

ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

single-displacement reaction

(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

soluble

of relatively high solubility; dissolving to a relatively large extent

solubility

the extent to which a substance may be dissolved in water, or any solvent

strong acid

acid that reacts completely when dissolved in water to yield hydronium ions

strong base

base that reacts completely when dissolved in water to yield hydroxide ions

weak acid

acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

weak base

base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

## Reaction Stoichiometry

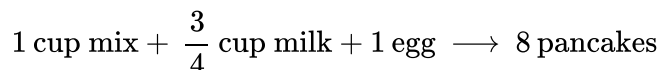
By the end of this section, you will be able to:

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning “element”) and *metron* (meaning “measure”). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Food preparation, for example, offers an appropriate comparison. A recipe for making eight pancakes calls for 1 cup pancake mix,  $\frac{3}{4}$  cup milk, and one egg. The “equation” representing the preparation of pancakes per this recipe is

**Equation:**



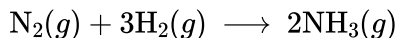
If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

**Equation:**

$$24 \text{ ~~pancakes~~} \times \frac{1 \text{ egg}}{8 \text{ ~~pancakes~~}} = 3 \text{ eggs}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

**Equation:**



This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

**Equation:**

$$\frac{2 \text{ NH}_3 \text{ molecules}}{3 \text{ H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}}$$

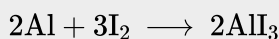
These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

**Example:**

**Moles of Reactant Required in a Reaction**

How many moles of  $I_2$  are required to react with 0.429 mol of Al according to the following equation (see [link](#))?

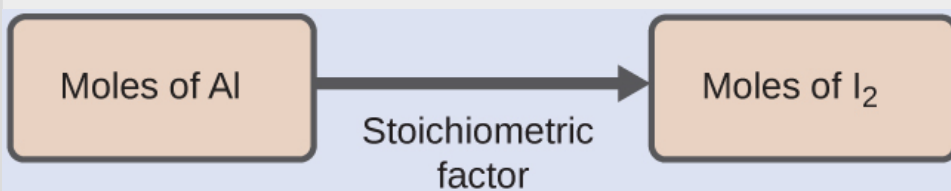
**Equation:**



Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

**Solution**

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is  $\frac{3 \text{ mol } I_2}{2 \text{ mol Al}}$ . The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



**Equation:**

$$\begin{aligned} \text{mol } I_2 &= 0.429 \text{ mol Al} \times \frac{3 \text{ mol } I_2}{2 \text{ mol Al}} \\ &= 0.644 \text{ mol } I_2 \end{aligned}$$

**Check Your Learning**

How many moles of  $Ca(OH)_2$  are required to react with 1.36 mol of  $H_3PO_4$  to produce  $Ca_3(PO_4)_2$  according to the equation  $3Ca(OH)_2 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$ ?

**Note:**

**Answer:**

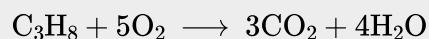
2.04 mol

**Example:**

**Number of Product Molecules Generated by a Reaction**

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

**Equation:**



**Solution**

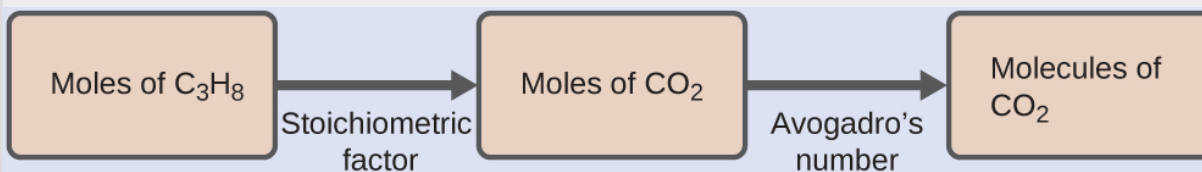
The approach here is the same as for [\[link\]](#), though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

**Equation:**

$$\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



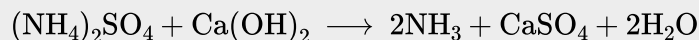
**Equation:**

$$0.75 \text{ mol C}_3\text{H}_8 \times \frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \times \frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{1 \text{ mol CO}_2} = 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

**Check Your Learning**

How many  $\text{NH}_3$  molecules are produced by the reaction of 4.0 mol of  $\text{Ca(OH)}_2$  according to the following equation:

**Equation:**



**Note:**

**Answer:**

$4.8 \times 10^{24}$   $\text{NH}_3$  molecules

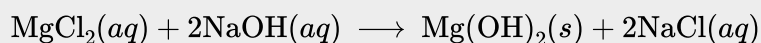
These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

### Example:

#### Relating Masses of Reactants and Products

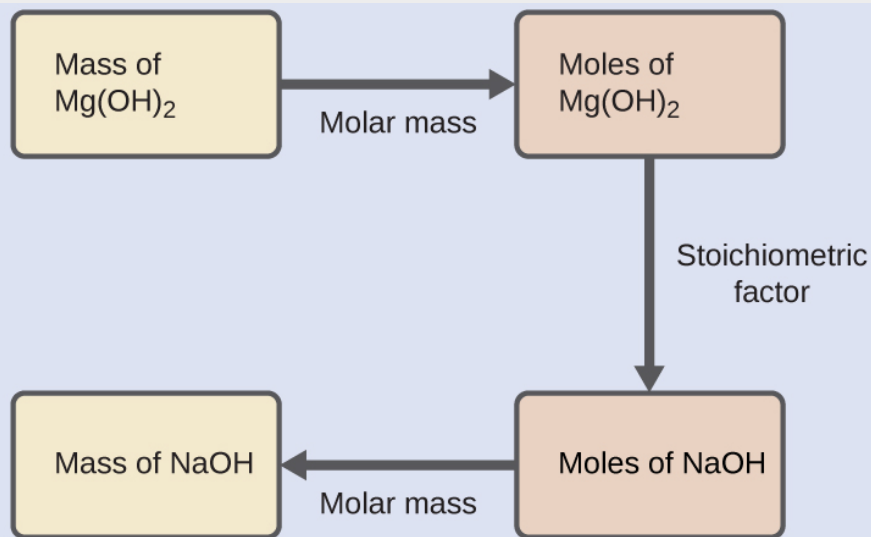
What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, Mg(OH)<sub>2</sub>] by the following reaction?

#### Equation:



#### Solution

The approach used previously in [\[link\]](#) and [\[link\]](#) is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



#### Equation:

$$16 \text{ g Mg}(\text{OH})_2 \times \frac{1 \text{ mol Mg}(\text{OH})_2}{58.3 \text{ g Mg}(\text{OH})_2} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol Mg}(\text{OH})_2} \times \frac{40.0 \text{ g NaOH}}{1 \text{ mol NaOH}} = 22 \text{ g NaOH}$$

#### Check Your Learning

What mass of gallium oxide,  $\text{Ga}_2\text{O}_3$ , can be prepared from 29.0 g of gallium metal? The equation for the reaction is  $4\text{Ga} + 3\text{O}_2 \rightarrow 2\text{Ga}_2\text{O}_3$ .

**Note:**

**Answer:**

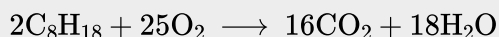
39.0 g

**Example:**

### Relating Masses of Reactants

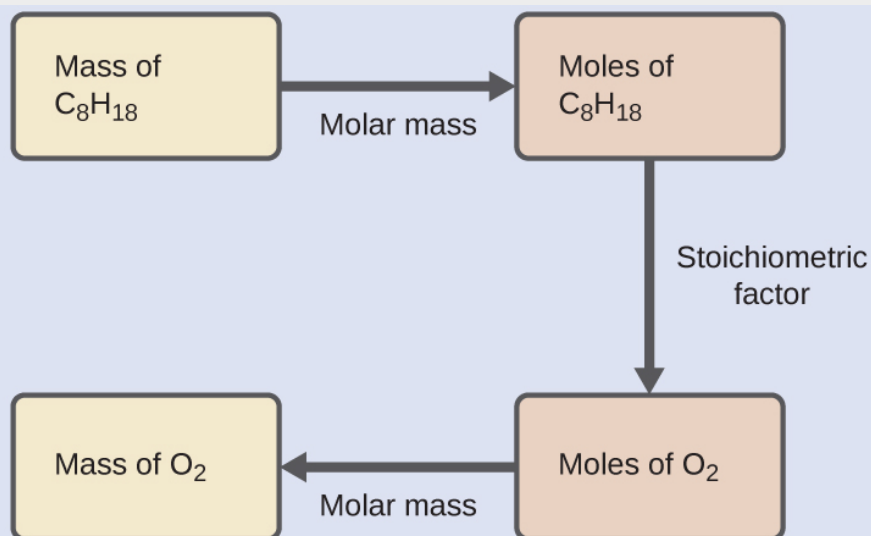
What mass of oxygen gas,  $\text{O}_2$ , from the air is consumed in the combustion of 702 g of octane,  $\text{C}_8\text{H}_{18}$ , one of the principal components of gasoline?

**Equation:**



**Solution**

The approach required here is the same as for the [link](#), differing only in that the provided and requested masses are both for reactant species.



**Equation:**

$$702 \text{ g C}_8\text{H}_{18} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.23 \text{ g C}_8\text{H}_{18}} \times \frac{25 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} \times \frac{32.00 \text{ g O}_2}{\text{mol O}_2} = 2.46 \times 10^3 \text{ g O}_2$$

### Check Your Learning

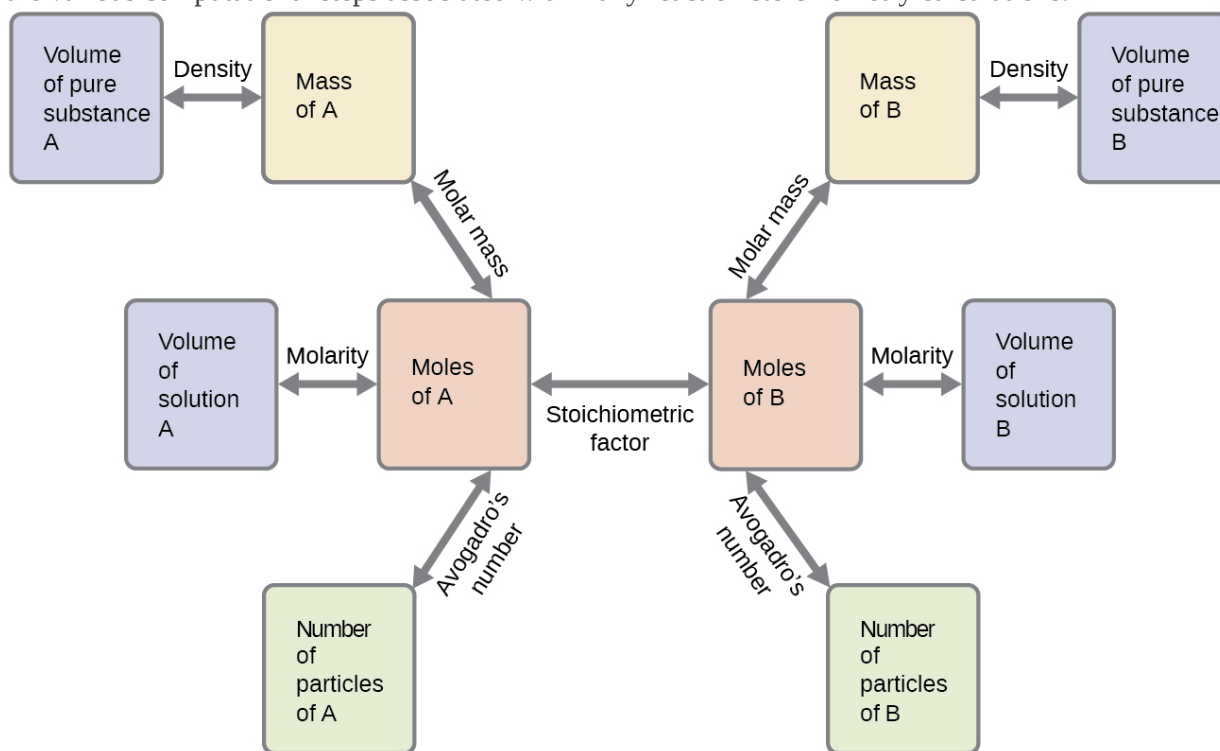
What mass of  $\text{CO}$  is required to react with 25.13 g of  $\text{Fe}_2\text{O}_3$  according to the equation  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ ?

**Note:**

**Answer:**

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. [\[link\]](#) provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.



The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

**Note:**

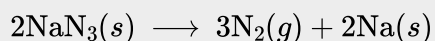
**Airbags**

Airbags ([\[link\]](#)) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of



sodium azide,  $\text{NaN}_3$ . When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of  $\text{NaN}_3$  to initiate its decomposition:

**Equation:**



This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second ( $\sim 0.03\text{--}0.1$  s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass ( $\sim 100$  g) of  $\text{NaN}_3$  will generate approximately 50 L of  $\text{N}_2$ .



Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

## Key Concepts and Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:**

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

- (a) The number of moles and the mass of chlorine,  $\text{Cl}_2$ , required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
- (b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
- (c) The number of moles and the mass of sodium nitrate,  $\text{NaNO}_3$ , required to produce 128 g of oxygen. ( $\text{NaNO}_2$  is the other product.)
- (d) The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.
- (e) The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. ( $\text{CO}_2$  is the other product.)
- (f)

The number of moles and the mass of  $\text{Br}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{Br}$  formed by the reaction of 12.85 g of  $\text{H}_2\text{C}=\text{CH}_2$  with an excess of  $\text{Br}_2$ .

### Exercise:

**Problem:** Determine the number of moles and the mass requested for each reaction in [\[link\]](#).

### Solution:

(a) 0.435 mol Na, 0.217 mol  $\text{Cl}_2$ , 15.4 g  $\text{Cl}_2$ ; (b) 0.005780 mol  $\text{HgO}$ ,  $2.890 \times 10^{-3}$  mol  $\text{O}_2$ ,  $9.248 \times 10^{-2}$  g  $\text{O}_2$ ; (c) 8.00 mol  $\text{NaNO}_3$ ,  $6.8 \times 10^2$  g  $\text{NaNO}_3$ ; (d) 1665 mol  $\text{CO}_2$ , 73.3 kg  $\text{CO}_2$ ; (e) 18.86 mol  $\text{CuO}$ , 2.330 kg  $\text{CuCO}_3$ ; (f) 0.4580 mol  $\text{C}_2\text{H}_4\text{Br}_2$ , 86.05 g  $\text{C}_2\text{H}_4\text{Br}_2$

### Exercise:

### Problem:

Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

- (a) The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce  $\text{MgCl}_2$  and  $\text{H}_2$ .
- (b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver(I) oxide.
- (c) The number of moles and the mass of magnesium carbonate,  $\text{MgCO}_3$ , required to produce 283 g of carbon dioxide. ( $\text{MgO}$  is the other product.)
- (d) The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene,  $\text{C}_2\text{H}_2$ , in an excess of oxygen.

(e) The number of moles and the mass of barium peroxide,  $\text{BaO}_2$ , needed to produce 2.500 kg of barium oxide,  $\text{BaO}$  ( $\text{O}_2$  is the other product.)

(f)

The number of moles and the mass of  $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$  required to react with  $\text{H}_2\text{O}$  to produce 9.55 g of  $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C}- & \text{C}-\text{O}-\text{H} \\ | & | \\ \text{H} & \text{H} \end{array}$ .

**Exercise:**

**Problem:** Determine the number of moles and the mass requested for each reaction in [\[link\]](#).

---

**Solution:**

(a) 0.0686 mol Mg, 1.67 g Mg; (b)  $2.701 \times 10^{-3}$  mol  $\text{O}_2$ , 0.08644 g  $\text{O}_2$ ; (c) 6.43 mol  $\text{MgCO}_3$ , 542 g  $\text{MgCO}_3$  (d) 713 mol  $\text{H}_2\text{O}$ , 12.8 kg  $\text{H}_2\text{O}$ ; (e) 16.31 mol  $\text{BaO}_2$ , 2762 g  $\text{BaO}_2$ ; (f) 0.207 mol  $\text{C}_2\text{H}_4$ , 5.81 g  $\text{C}_2\text{H}_4$

**Exercise:**

**Problem:**

$\text{H}_2$  is produced by the reaction of 118.5 mL of a 0.8775-M solution of  $\text{H}_3\text{PO}_4$  according to the following equation:  $2\text{Cr} + 2\text{H}_3\text{PO}_4 \longrightarrow 3\text{H}_2 + 2\text{CrPO}_4$ .

(a) Outline the steps necessary to determine the number of moles and mass of  $\text{H}_2$ .

(b) Perform the calculations outlined.

**Exercise:**

**Problem:**

Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of  $\text{HCl}$  according to the following equation:  $2\text{Ga} + 6\text{HCl} \longrightarrow 2\text{GaCl}_3 + 3\text{H}_2$ .

(a) Outline the steps necessary to determine the number of moles and mass of gallium chloride.

(b) Perform the calculations outlined.

---

**Solution:**

(a) volume  $\text{HCl}$  solution  $\longrightarrow$  mol  $\text{HCl}$   $\longrightarrow$  mol  $\text{GaCl}_3$ ; (b) 1.25 mol  $\text{GaCl}_3$ ,  $2.2 \times 10^2$  g  $\text{GaCl}_3$

**Exercise:**

**Problem:**

$\text{I}_2$  is produced by the reaction of 0.4235 mol of  $\text{CuCl}_2$  according to the following equation:  $2\text{CuCl}_2 + 4\text{KI} \longrightarrow 2\text{CuI} + 4\text{KCl} + \text{I}_2$ .

(a) How many molecules of  $\text{I}_2$  are produced?

(b) What mass of  $I_2$  is produced?

**Exercise:**

**Problem:**

Silver is often extracted from ores such as  $K[Ag(CN)_2]$  and then recovered by the reaction



(a) How many molecules of  $Zn(CN)_2$  are produced by the reaction of 35.27 g of  $K[Ag(CN)_2]$ ?

(b) What mass of  $Zn(CN)_2$  is produced?

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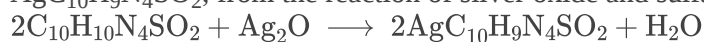
**Solution:**

(a)  $5.337 \times 10^{22}$  molecules; (b) 10.41 g  $Zn(CN)_2$

**Exercise:**

**Problem:**

What mass of silver oxide,  $Ag_2O$ , is required to produce 25.0 g of silver sulfadiazine,  $AgC_{10}H_9N_4SO_2$ , from the reaction of silver oxide and sulfadiazine?



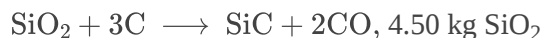
**Exercise:**

**Problem:**

Carborundum is silicon carbide,  $SiC$ , a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand,  $SiO_2$ , with carbon at high temperature. Carbon monoxide,  $CO$ , is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much  $SiO_2$  is required to produce 3.00 kg of  $SiC$ .

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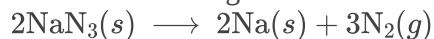
**Solution:**



**Exercise:**

**Problem:**

Automotive air bags inflate when a sample of sodium azide,  $NaN_3$ , is very rapidly decomposed.

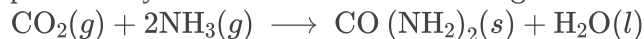


What mass of sodium azide is required to produce 2.6  $ft^3$  (73.6 L) of nitrogen gas with a density of 1.25 g/L?

**Exercise:**

**Problem:**

Urea,  $CO(NH_2)_2$ , is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the  $CO_2$  produced by combustion of  $1.00 \times 10^3$  kg of carbon followed by the reaction?



**Solution:**

$$5.00 \times 10^3 \text{ kg}$$

**Exercise:****Problem:**

In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of  $\text{Na}_2\text{CO}_3$  was quickly spread on the area and  $\text{CO}_2$  was released by the reaction. Was sufficient  $\text{Na}_2\text{CO}_3$  used to neutralize all of the acid?

**Exercise:****Problem:**

A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

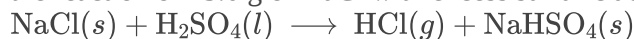
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**Solution:**

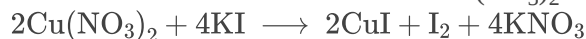
$$1.28 \times 10^5 \text{ g CO}_2$$

**Exercise:****Problem:**

What volume of 0.750 M hydrochloric acid solution can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with excess sulfuric acid?

**Exercise:****Problem:**

What volume of a 0.2089 M KI solution contains enough KI to react exactly with the  $\text{Cu}(\text{NO}_3)_2$  in 43.88 mL of a 0.3842 M solution of  $\text{Cu}(\text{NO}_3)_2$ ?



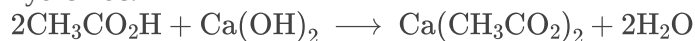
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**Solution:**

161.4 mL KI solution

**Exercise:****Problem:**

A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

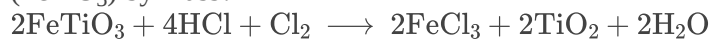


What mass of  $\text{Ca}(\text{OH})_2$  is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

**Exercise:**

**Problem:**

The toxic pigment called white lead,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , has been replaced in white paints by rutile,  $\text{TiO}_2$ . How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ( $\text{FeTiO}_3$ ) by mass?

**Solution:**

176 g  $\text{TiO}_2$

**Glossary**

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

## Reaction Yields

By the end of this section, you will be able to:

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

## Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches ([link](#)):

**Equation:**



Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

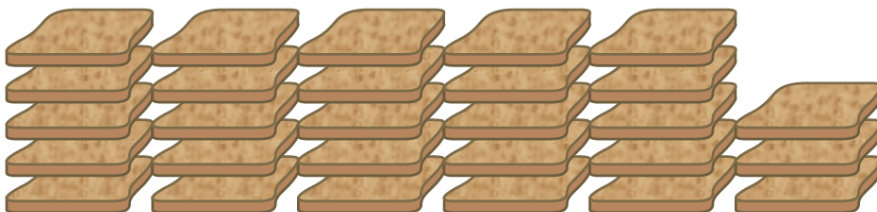
1 sandwich = 2 slices of bread + 1 slice of cheese



Provided with:

28 slices of bread

+ 11 slices of cheese



We can make:

11 sandwiches

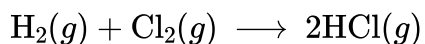
+ 6 slices bread left over



Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

**Equation:**



The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the **limiting reactant**, and the other substance is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of  $\text{H}_2$  and 2 moles of  $\text{Cl}_2$ . This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's



stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, complete reaction of the hydrogen would yield

**Equation:**

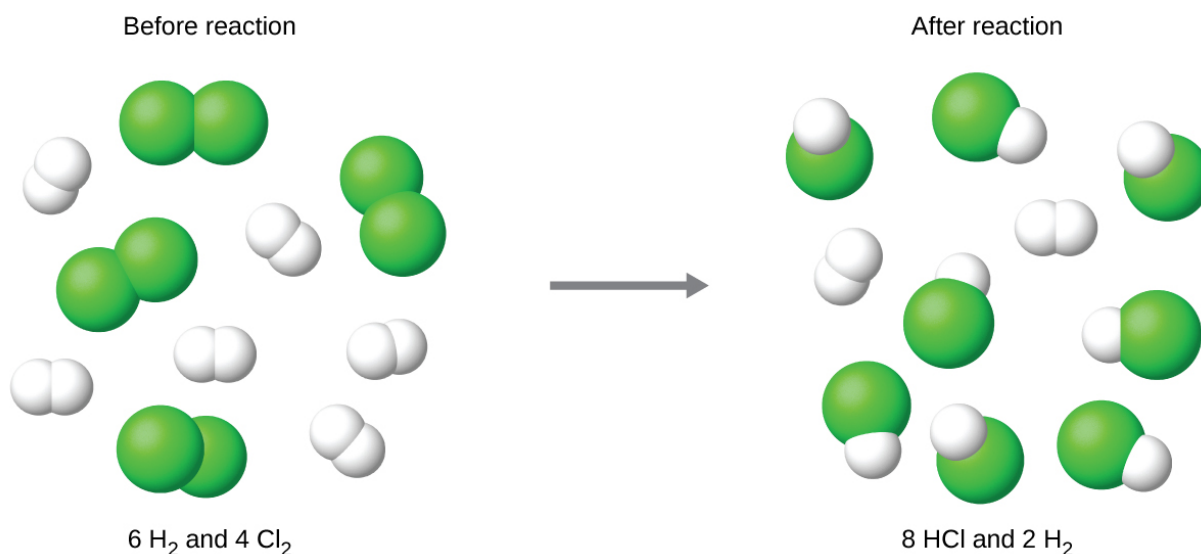
$$\text{mol HCl produced} = 3 \text{ mol H}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol H}_2} = 6 \text{ mol HCl}$$

Complete reaction of the provided chlorine would produce

**Equation:**

$$\text{mol HCl produced} = 2 \text{ mol Cl}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Cl}_2} = 4 \text{ mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant ([\[link\]](#)).



When H<sub>2</sub> and Cl<sub>2</sub> are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

**Note:**

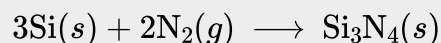
View this interactive [simulation](#) illustrating the concepts of limiting and excess reactants.

**Example:**

**Identifying the Limiting Reactant**

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

**Equation:**



Which is the limiting reactant when 2.00 g of Si and 1.50 g of N<sub>2</sub> react?

**Solution**

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

**Equation:**

$$\text{mol Si} = 2.00 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 0.0712 \text{ mol Si}$$

**Equation:**

$$\text{mol N}_2 = 1.50 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.02 \text{ g N}_2} = 0.0535 \text{ mol N}_2$$

The provided Si:N<sub>2</sub> molar ratio is:

**Equation:**

$$\frac{0.0712 \text{ mol Si}}{0.0535 \text{ mol N}_2} = \frac{1.33 \text{ mol Si}}{1 \text{ mol N}_2}$$

The stoichiometric Si:N<sub>2</sub> ratio is:

**Equation:**

$$\frac{3 \text{ mol Si}}{2 \text{ mol N}_2} = \frac{1.5 \text{ mol Si}}{1 \text{ mol N}_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

**Equation:**

$$\text{mol Si}_3\text{N}_4 \text{ produced} = 0.0712 \text{ mol Si} \times \frac{1 \text{ mol Si}_3\text{N}_4}{3 \text{ mol Si}} = 0.0237 \text{ mol Si}_3\text{N}_4$$

while the 0.0535 moles of nitrogen would produce

**Equation:**

$$\text{mol Si}_3\text{N}_4 \text{ produced} = 0.0535 \text{ mol N}_2 \times \frac{1 \text{ mol Si}_3\text{N}_4}{2 \text{ mol N}_2} = 0.0268 \text{ mol Si}_3\text{N}_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

**Check Your Learning**

Which is the limiting reactant when 5.00 g of H<sub>2</sub> and 10.0 g of O<sub>2</sub> react and form water?

**Note:**

**Answer:**

O<sub>2</sub>

## Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this chapter). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

**Equation:**

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

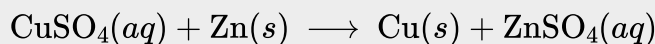
Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

**Example:**

**Calculation of Percent Yield**

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

**Equation:**



What is the percent yield?

**Solution**

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

**Equation:**

$$1.274 \text{ g CuSO}_4 \times \frac{1 \text{ mol CuSO}_4}{159.62 \text{ g CuSO}_4} \times \frac{1 \text{ mol Cu}}{1 \text{ mol CuSO}_4} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = 0.5072 \text{ g Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

**Equation:**

$$\text{percent yield} = \left( \frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100$$

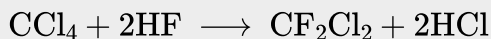
**Equation:**

$$\begin{aligned} \text{percent yield} &= \left( \frac{0.392 \text{ g Cu}}{0.5072 \text{ g Cu}} \right) \times 100 \\ &= 77.3\% \end{aligned}$$

### Check Your Learning

What is the percent yield of a reaction that produces 12.5 g of the gas Freon  $\text{CF}_2\text{Cl}_2$  from 32.9 g of  $\text{CCl}_4$  and excess HF?

**Equation:**



**Note:**

**Answer:**

48.3%

**Note:****Green Chemistry and Atom Economy**

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the “Twelve Principles of Green Chemistry” (see details at this [website](#)). One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

**Equation:**

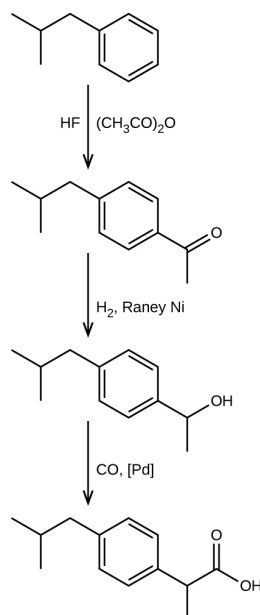
$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach ([link](#)). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency’s Greener Synthetic Pathways Award in 1997.



(a)



(b)

(a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

## Key Concepts and Summary

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant. The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

## Key Equations

$$\text{percent yield} = \left( \frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

The following quantities are placed in a container:  $1.5 \times 10^{24}$  atoms of hydrogen, 1.0 mol of sulfur, and 88.0 g of diatomic oxygen.

- (a) What is the total mass in grams for the collection of all three elements?
- (b) What is the total number of moles of atoms for the three elements?
- (c) If the mixture of the three elements formed a compound with molecules that contain two hydrogen atoms, one sulfur atom, and four oxygen atoms, which substance is consumed first?
- (d) How many atoms of each remaining element would remain unreacted in the change described in (c)?

### Exercise:

#### Problem:

What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

---

#### Solution:

The limiting reactant is  $\text{Cl}_2$ .

### Exercise:

#### Problem:

Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?

### Exercise:

#### Problem:

A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

---

#### Solution:

Percent yield = 31%

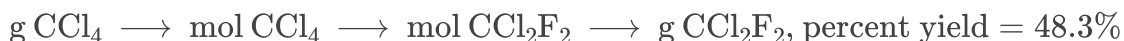
**Exercise:****Problem:**

A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

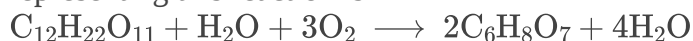
**Exercise:****Problem:**

Freon-12,  $\text{CCl}_2\text{F}_2$ , is prepared from  $\text{CCl}_4$  by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of  $\text{CCl}_2\text{F}_2$  from 32.9 g of  $\text{CCl}_4$ . Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

---

**Solution:****Exercise:****Problem:**

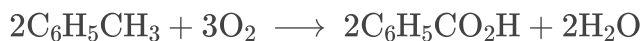
Citric acid,  $\text{C}_6\text{H}_8\text{O}_7$ , a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is



What mass of citric acid is produced from exactly 1 metric ton ( $1.000 \times 10^3$  kg) of sucrose if the yield is 92.30%?

**Exercise:****Problem:**

Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ , is oxidized by air under carefully controlled conditions to benzoic acid,  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ , which is used to prepare the food preservative sodium benzoate,  $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$ . What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid?



---

**Solution:**

$$\text{percent yield} = 91.3\%$$

**Exercise:**

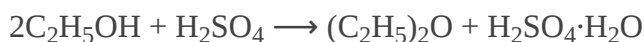


**Problem:**

In a laboratory experiment, the reaction of 3.0 mol of  $\text{H}_2$  with 2.0 mol of  $\text{I}_2$  produced 1.0 mol of  $\text{HI}$ . Determine the theoretical yield in grams and the percent yield for this reaction.

**Exercise:****Problem:**

Outline the steps needed to solve the following problem, then do the calculations. Ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , which was originally used as an anesthetic but has been replaced by safer and more effective medications, is prepared by the reaction of ethanol with sulfuric acid.



What is the percent yield of ether if 1.17 L ( $d = 0.7134 \text{ g/mL}$ ) is isolated from the reaction of 1.500 L of  $\text{C}_2\text{H}_5\text{OH}$  ( $d = 0.7894 \text{ g/mL}$ )?

---

**Solution:**

Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield; 87.6%

**Exercise:****Problem:**

Outline the steps needed to determine the limiting reactant when 30.0 g of propane,  $\text{C}_3\text{H}_8$ , is burned with 75.0 g of oxygen.

Determine the limiting reactant.

**Exercise:****Problem:**

Outline the steps needed to determine the limiting reactant when 0.50 mol of  $\text{Cr}$  and 0.75 mol of  $\text{H}_3\text{PO}_4$  react according to the following chemical equation.



Determine the limiting reactant.

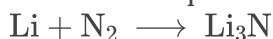
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**Solution:**

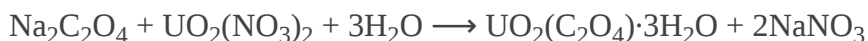
The conversion needed is  $\text{mol Cr} \longrightarrow \text{mol H}_3\text{PO}_4$ . Then compare the amount of  $\text{Cr}$  to the amount of acid present.  $\text{Cr}$  is the limiting reactant.

**Exercise:****Problem:**

What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?

**Exercise:****Problem:**

Uranium can be isolated from its ores by dissolving it as  $\text{UO}_2(\text{NO}_3)_2$ , then separating it as solid  $\text{UO}_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$ . Addition of 0.4031 g of sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , to a solution containing 1.481 g of uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2$ , yields 1.073 g of solid  $\text{UO}_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$ .



Determine the limiting reactant and the percent yield of this reaction.

---

**Solution:**

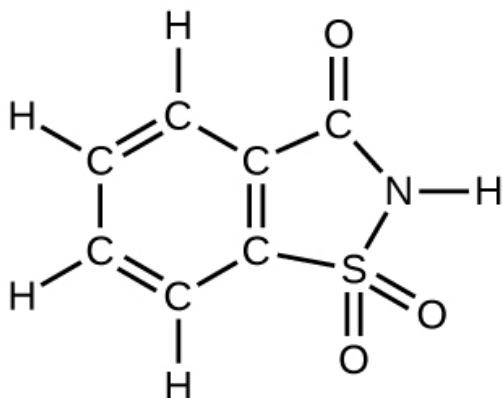
$\text{Na}_2\text{C}_2\text{O}_4$  is the limiting reactant. percent yield = 86.56%

**Exercise:****Problem:**

How many molecules of  $\text{C}_2\text{H}_4\text{Cl}_2$  can be prepared from 15  $\text{C}_2\text{H}_4$  molecules and 8  $\text{Cl}_2$  molecules?

**Exercise:****Problem:**

How many molecules of the sweetener saccharin can be prepared from 30 C atoms, 25 H atoms, 12 O atoms, 8 S atoms, and 14 N atoms?



---

**Solution:**

Only four molecules can be made.

**Exercise:****Problem:**

The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.

(a) What is the limiting reactant when 0.200 mol of  $P_4$  and 0.200 mol of  $O_2$  react according to  $P_4 + 5O_2 \longrightarrow P_4O_{10}$

(b) Calculate the percent yield if 10.0 g of  $P_4O_{10}$  is isolated from the reaction.

**Exercise:****Problem:**

Would you agree to buy 1 trillion (1,000,000,000,000) gold atoms for \$5? Explain why or why not. Find the current price of gold at <http://money.cnn.com/data/commodities/> (1 troy ounce = 31.1 g)

---

**Solution:**

This amount cannot be weighted by ordinary balances and is worthless.

**Glossary**

actual yield

amount of product formed in a reaction

excess reactant

reactant present in an amount greater than required by the reaction stoichiometry

limiting reactant

reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

percent yield

measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

theoretical yield

amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

## Quantitative Chemical Analysis

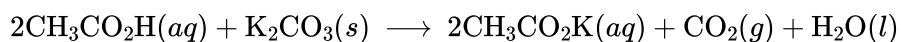
By the end of this section, you will be able to:

- Describe the fundamental aspects of titrations and gravimetric analysis.
- Perform stoichiometric calculations using typical titration and gravimetric data.

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate,  $\text{K}_2\text{CO}_3$ , which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

**Equation:**

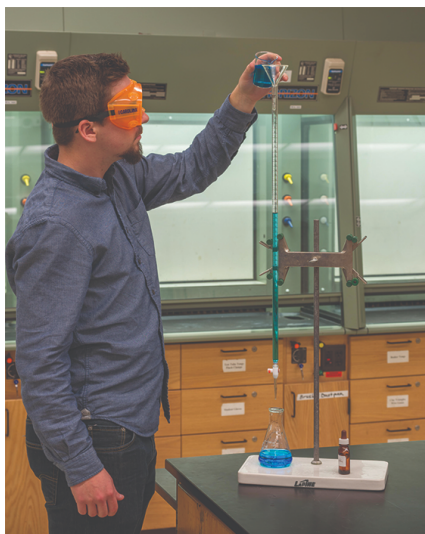


The bubbling was due to the production of  $\text{CO}_2$ .

The test of vinegar with potassium carbonate is one type of **quantitative analysis**—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

## Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as **titration analysis**. A typical titration analysis involves the use of a **buret** ([link](#)) to make incremental additions of a solution containing a known concentration of some substance (the **titrant**) to a sample solution containing the substance whose concentration is to be measured (the **analyte**). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the **equivalence point** of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called **indicators** are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the **end point**. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.



(a)



(b)

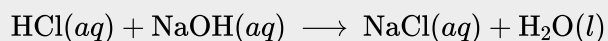
(a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.01 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

### Example:

#### Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

#### Equation:

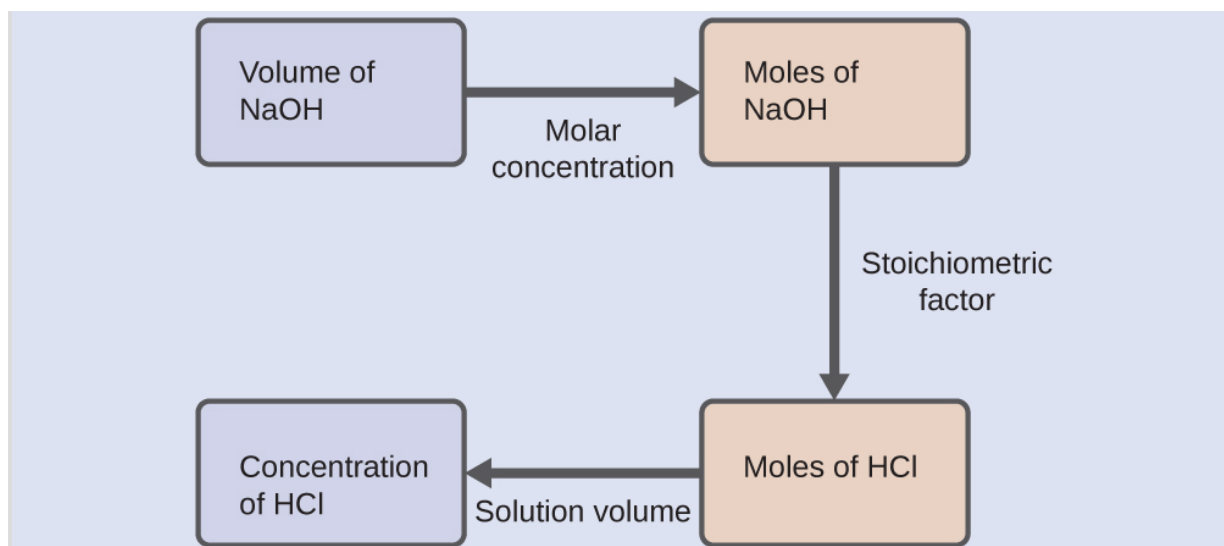


What is the molarity of the HCl?

#### Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

**Equation:**

$$35.23 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 8.81 \times 10^{-3} \text{ mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

**Equation:**

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$

$$M = 0.176 \text{ M}$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *millimoles* of solute per *milliliter* of solution:

**Equation:**

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3 \text{ mmol}}{\text{mol}}}{\frac{10^3 \text{ mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

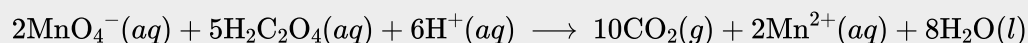
**Equation:**

$$\frac{35.23 \text{ mL NaOH} \times \frac{0.250 \text{ mmol NaOH}}{\text{mL NaOH}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{50.00 \text{ mL solution}} = 0.176 \text{ M HCl}$$

### Check Your Learning

A 20.00-mL sample of aqueous oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , was titrated with a 0.09113-M solution of potassium permanganate,  $\text{KMnO}_4$ .

**Equation:**



A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

**Note:**

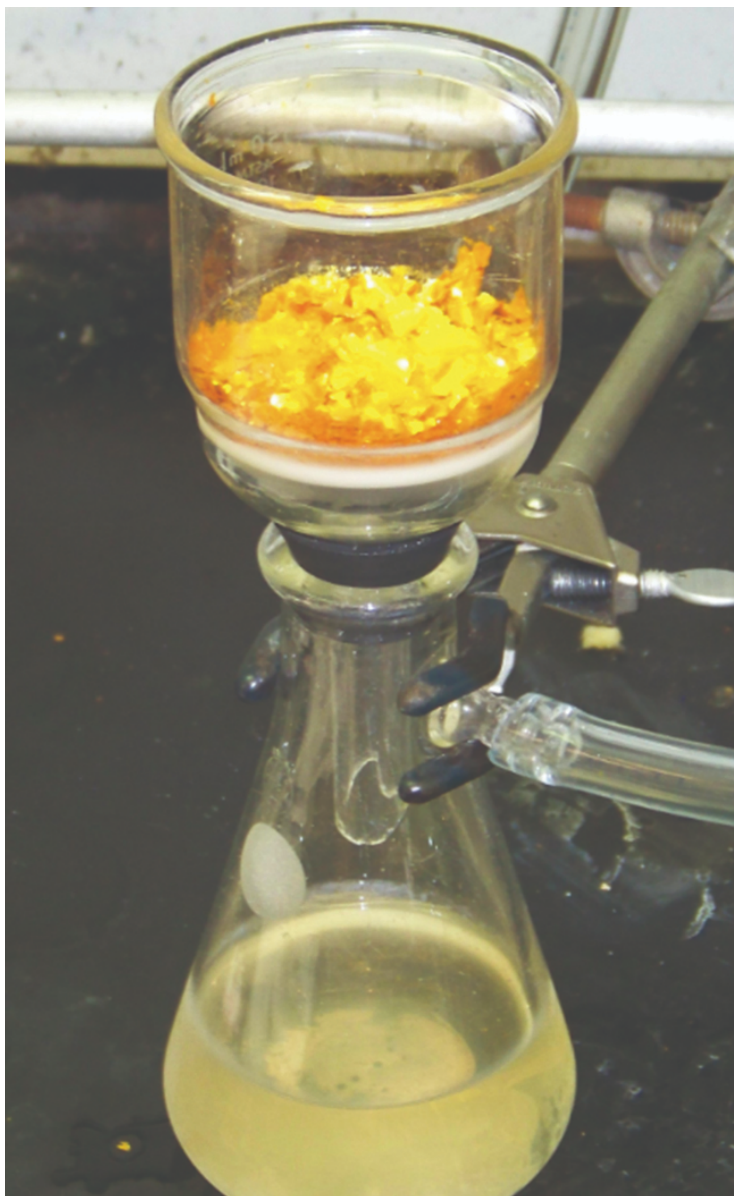
**Answer:**

0.2648 M

## Gravimetric Analysis

A **gravimetric analysis** is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample. Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration. Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory.

The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes. For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water. Also common are gravimetric techniques in which the analyte is subjected to a precipitation reaction of the sort described earlier in this chapter. The precipitate is typically isolated from the reaction mixture by filtration, carefully dried, and then weighed ([link](#)). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.



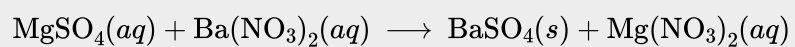
Precipitate may be removed from a reaction mixture by filtration.

**Example:**

**Gravimetric Analysis**

A 0.4550-g solid mixture containing  $\text{MgSO}_4$  is dissolved in water and treated with an excess of  $\text{Ba}(\text{NO}_3)_2$ , resulting in the precipitation of 0.6168 g of  $\text{BaSO}_4$ .

**Equation:**

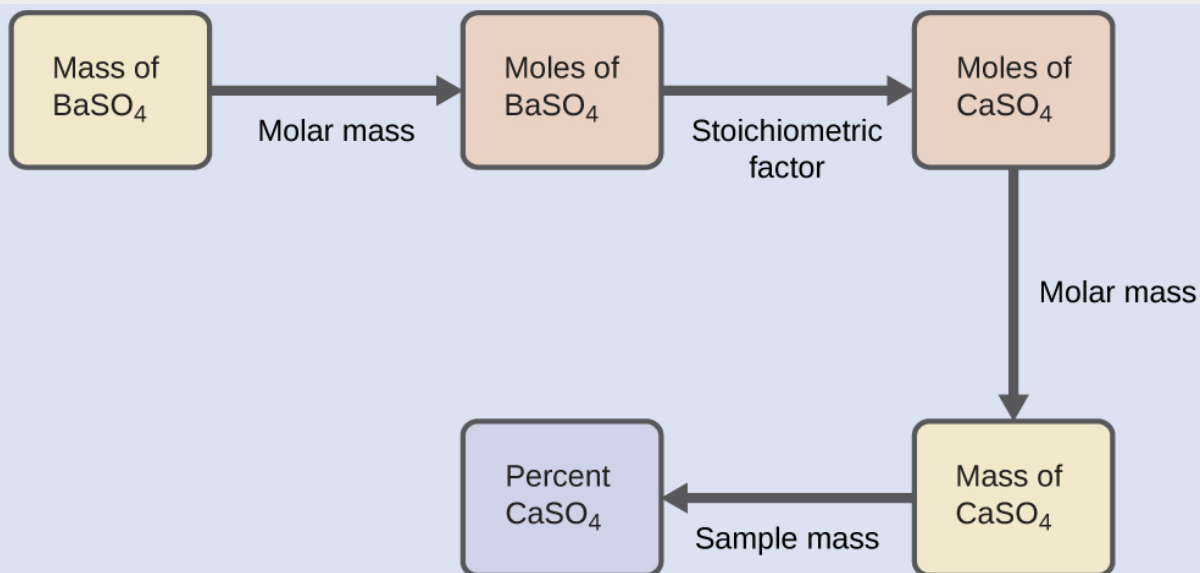




What is the concentration (mass percent) of  $\text{MgSO}_4$  in the mixture?

**Solution**

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of  $\text{BaSO}_4$  and  $\text{MgSO}_4$  through their stoichiometric factor. Once the mass of  $\text{MgSO}_4$  is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



The mass of  $\text{MgSO}_4$  that would yield the provided precipitate mass is

**Equation:**

$$0.6168 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.43 \text{ g BaSO}_4} \times \frac{1 \text{ mol MgSO}_4}{1 \text{ mol BaSO}_4} \times \frac{120.37 \text{ g MgSO}_4}{1 \text{ mol MgSO}_4} = 0.3181 \text{ g MgSO}_4$$

The concentration of  $\text{MgSO}_4$  in the sample mixture is then calculated to be

**Equation:**

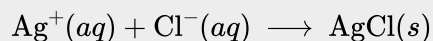
$$\text{percent MgSO}_4 = \frac{\text{mass MgSO}_4}{\text{mass sample}} \times 100\%$$

$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

**Check Your Learning**

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of  $\text{AgCl}$  when treated with excess  $\text{Ag}^+$ ?

**Equation:**

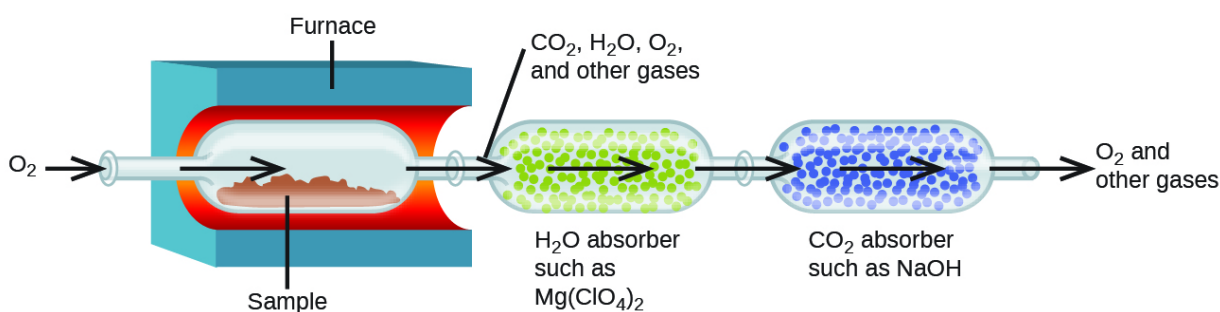


**Note:**

**Answer:**

23.76%

The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as **combustion analysis**. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product ([link](#)). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.



This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

### Example:

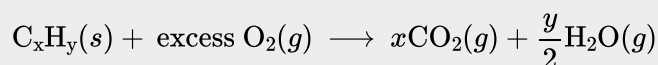
#### Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of  $\text{CO}_2$  and 0.00161 g of  $\text{H}_2\text{O}$ . What is the empirical formula of polyethylene?

#### Solution

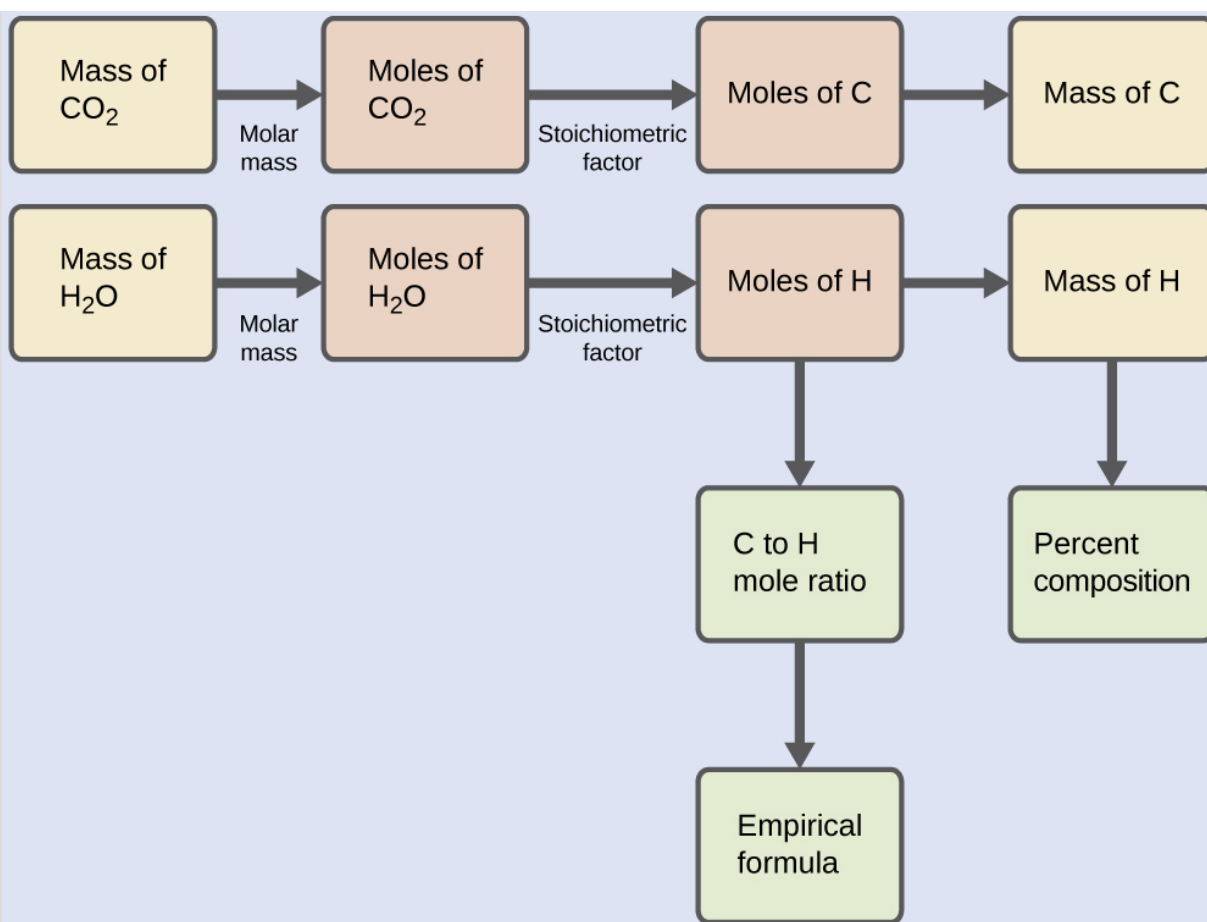
The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

#### Equation:



Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts  $x$  and  $y$  are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:



**Equation:**

$$\text{mol C} = 0.00394 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g}} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 8.95 \times 10^{-5} \text{ mol C}$$

$$\text{mol H} = 0.00161 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 1.79 \times 10^{-4} \text{ mol H}$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is

**Equation:**

$$\frac{\text{mol H}}{\text{mol C}} = \frac{1.79 \times 10^{-4} \text{ mol H}}{8.95 \times 10^{-5} \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

and the empirical formula for polyethylene is CH<sub>2</sub>.

### Check Your Learning

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO<sub>2</sub> and 0.00148 g of H<sub>2</sub>O in a combustion analysis. What is the empirical formula for polystyrene?

**Note:**

**Answer:**

## Key Concepts and Summary

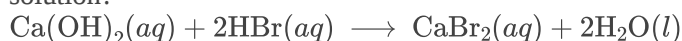
The stoichiometry of chemical reactions may serve as the basis for quantitative chemical analysis methods. Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction. Gravimetric analysis involves separating the analyte from the sample by a physical or chemical process, determining its mass, and then calculating its concentration in the sample based on the stoichiometry of the relevant process. Combustion analysis is a gravimetric method used to determine the elemental composition of a compound by collecting and weighing the gaseous products of its combustion.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

What volume of 0.0105-M HBr solution is required to titrate 125 mL of a 0.0100-M  $\text{Ca}(\text{OH})_2$  solution?



### Exercise:

#### Problem:

Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 M NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

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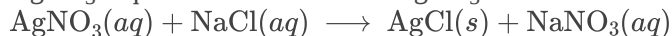
#### Solution:

$$3.4 \times 10^{-3} \text{ M H}_2\text{SO}_4$$

### Exercise:

#### Problem:

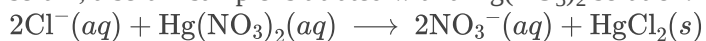
What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 M  $\text{AgNO}_3$  requires 20.22 mL of the  $\text{AgNO}_3$  solution to reach the end point?



### Exercise:

#### Problem:

In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a  $\text{Hg}(\text{NO}_3)_2$  solution.



What is the  $\text{Cl}^-$  concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of  $8.25 \times 10^{-4} \text{ M Hg(NO}_3)_2(aq)$  to reach the end point?

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**Solution:**

$$9.6 \times 10^{-3} \text{ M Cl}^-$$

**Exercise:**

**Problem:**

Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCl to reach the end point?

**Exercise:**

**Problem:**

A sample of gallium bromide,  $\text{GaBr}_3$ , weighing 0.165 g was dissolved in water and treated with silver nitrate,  $\text{AgNO}_3$ , resulting in the precipitation of 0.299 g  $\text{AgBr}$ . Use these data to compute the %Ga (by mass)  $\text{GaBr}_3$ .

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**Solution:**

$$22.4\%$$

**Exercise:**

**Problem:**

The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of  $\text{CO}_2$ . Determine its empirical and molecular formulas.

**Exercise:**

**Problem:**

A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of  $\text{B}_2\text{O}_3$ . What are the empirical and molecular formulas of the compound?

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**Solution:**

The empirical formula is  $\text{BH}_3$ . The molecular formula is  $\text{B}_2\text{H}_6$ .

**Exercise:**

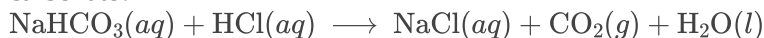
**Problem:**

Sodium bicarbonate (baking soda),  $\text{NaHCO}_3$ , can be purified by dissolving it in hot water ( $60^\circ\text{C}$ ), filtering to remove insoluble impurities, cooling to  $0^\circ\text{C}$  to precipitate solid  $\text{NaHCO}_3$ , and then filtering to remove the solid, leaving soluble impurities in solution. Any  $\text{NaHCO}_3$  that remains in solution is not recovered. The solubility of  $\text{NaHCO}_3$  in hot water of  $60^\circ\text{C}$  is 164 g/L. Its solubility in cold water of  $0^\circ\text{C}$  is 69 g/L. What is the percent yield of  $\text{NaHCO}_3$  when it is purified by this method?

**Exercise:**

**Problem:**

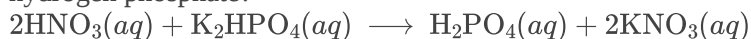
What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

**Solution:**

49.6 mL

**Exercise:****Problem:**

What volume of 0.08892 *M* HNO<sub>3</sub> is required to react completely with 0.2352 g of potassium hydrogen phosphate?

**Exercise:****Problem:**

What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

**Solution:**

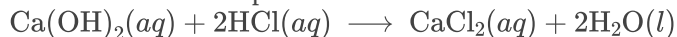
13.64 mL

**Exercise:****Problem:**

What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H<sub>2</sub>SO<sub>4</sub> concentration of  $1.23 \times 10^{-4}$  *M*.

**Exercise:****Problem:**

A sample of solid calcium hydroxide, Ca(OH)<sub>2</sub>, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with  $5.00 \times 10^{-2}$  *M* HCl requires 36.6 mL of the acid to reach the end point.



What is the molarity?

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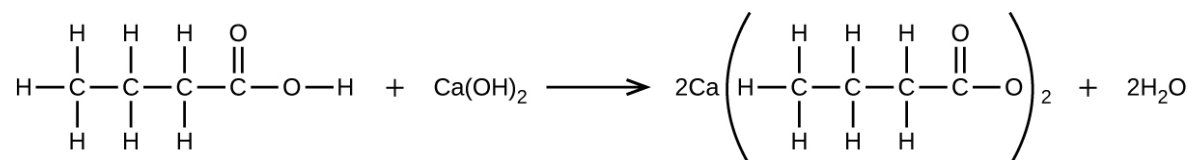
**Solution:**

0.0122 *M*

**Exercise:**

**Problem:**

What mass of  $\text{Ca}(\text{OH})_2$  will react with 25.0 g of butanoic to form the preservative calcium butanoate according to the equation?

**Exercise:****Problem:**

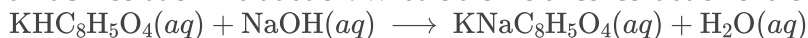
How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of  $\text{H}_3\text{PO}_4$ ?

**Solution:**

34.99 mL KOH

**Exercise:****Problem:**

Potassium hydrogen phthalate,  $\text{KHC}_8\text{H}_5\text{O}_4$ , or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of  $\text{KHC}_8\text{H}_5\text{O}_4$  reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

**Exercise:****Problem:**

The reaction of  $\text{WCl}_6$  with Al at  $\sim 400^\circ\text{C}$  gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 *M* NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

**Solution:**

The empirical formula is  $\text{WCl}_4$ .

**Glossary**

analyte

chemical species of interest

buret

device used for the precise delivery of variable liquid volumes, such as in a titration analysis

combustion analysis

gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

end point

measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

equivalence point

volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

gravimetric analysis

quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

indicator

substance added to the sample in a titration analysis to permit visual detection of the end point

quantitative analysis

the determination of the amount or concentration of a substance in a sample

titrant

solution containing a known concentration of substance that will react with the analyte in a titration analysis

titration analysis

quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample



## Introduction

class="introduction"

- Gas Pressure
- Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- Effusion and Diffusion of Gases
- The Kinetic-Molecular Theory
- Non-Ideal Gas Behavior

The hot air  
inside these  
balloons is  
less dense  
than the  
surrounding  
cool air.

This results  
in a buoyant  
force that  
causes the  
balloons to  
rise when  
their guy  
lines are  
untied.

(credit:  
modification  
of work  
by Anthony  
Quintano)



We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities. Heated gases expand, which can make a hot air balloon rise ([\[link\]](#)) or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behavior, providing the first mathematical descriptions of the behavior of matter.

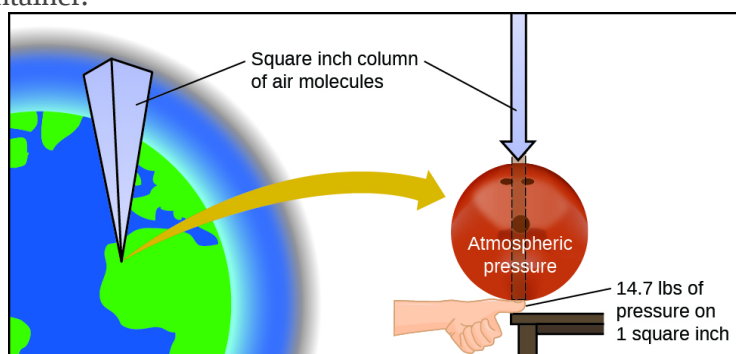
In this chapter, we will examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

## Gas Pressure

By the end of this section, you will be able to:

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears “pop” during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects ([link](#)). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.



The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

### Note:

A dramatic [illustration](#) of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

A smaller scale [demonstration](#) of this phenomenon is briefly explained.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth

has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is *twice* the usual pressure, and the sensation is unpleasant.

In general, **pressure** is defined as the force exerted on a given area:  $P = \frac{F}{A}$ . Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which would be more likely to fall through thin ice in [\[link\]](#)—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in<sup>2</sup>), so the pressure exerted by each foot is about 14 lb/in<sup>2</sup>:

**Equation:**

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in<sup>2</sup>, so the pressure exerted by each blade is about 30 lb/in<sup>2</sup>:

**Equation:**

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

**Equation:**

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2$$



(a)



(b)

Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a:

modification of work by Guido da Rozze; credit b:  
modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with  $1 \text{ Pa} = 1 \text{ N/m}^2$ , where N is the newton, a unit of force defined as  $1 \text{ kg m/s}^2$ . One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal ( $1 \text{ kPa} = 1000 \text{ Pa}$ ) or **bar** ( $1 \text{ bar} = 100,000 \text{ Pa}$ ). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere (atm)**, which originally represented the average sea level air pressure at the approximate latitude of Paris ( $45^\circ$ ). [\[link\]](#) provides some information on these and a few other common units for pressure measurements

Pressure Units	
Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	$1 \text{ Pa} = 1 \text{ N/m}^2$ recommended IUPAC unit
kilopascal (kPa)	$1 \text{ kPa} = 1000 \text{ Pa}$
pounds per square inch (psi)	air pressure at sea level is $\sim 14.7 \text{ psi}$
atmosphere (atm)	$1 \text{ atm} = 101,325 \text{ Pa} = 760 \text{ torr}$ air pressure at sea level is $\sim 1 \text{ atm}$
bar (bar, or b)	$1 \text{ bar} = 100,000 \text{ Pa}$ (exactly) commonly used in meteorology
millibar (mbar, or mb)	$1000 \text{ mbar} = 1 \text{ bar}$
inches of mercury (in. Hg)	$1 \text{ in. Hg} = 3386 \text{ Pa}$ used by aviation industry, also some weather reports
torr	$1 \text{ torr} = \frac{1}{760} \text{ atm}$ named after Evangelista Torricelli, inventor of the barometer

Pressure Units	
Unit Name and Abbreviation	Definition or Relation to Other Unit
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

### Example:

#### Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

- (a) torr
- (b) atm
- (c) kPa
- (d) mbar

#### Solution

This is a unit conversion problem. The relationships between the various pressure units are given in [\[link\]](#).

$$(a) 29.2 \text{ in Hg} \times \frac{25.4 \text{ mm}}{1 \text{ in}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 742 \text{ torr}$$

$$(b) 742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$$

$$(c) 742 \text{ torr} \times \frac{101.325 \text{ kPa}}{760 \text{ torr}} = 98.9 \text{ kPa}$$

$$(d) 98.9 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} \times \frac{1000 \text{ mbar}}{1 \text{ bar}} = 989 \text{ mbar}$$

#### Check Your Learning

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

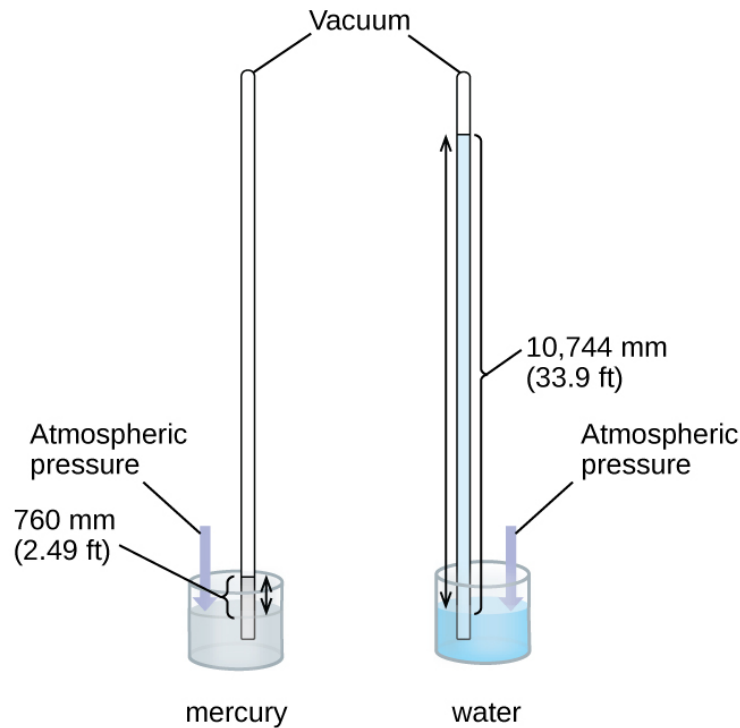
#### Note:

#### Answer:

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a **barometer** ([\[link\]](#)). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and

outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.



In a barometer, the height,  $h$ , of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be  $\frac{1}{13.6}$  as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The **torr** was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as **hydrostatic pressure**,  $p$ :

**Equation:**

$$p = h\rho g$$

where  $h$  is the height of the fluid,  $\rho$  is the density of the fluid, and  $g$  is acceleration due to gravity.

**Example:****Calculation of Barometric Pressure**

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = 13.6 g/cm<sup>3</sup>.

**Solution**

The hydrostatic pressure is given by  $p = h\rho g$ , with  $h = 760$  mm,  $\rho = 13.6$  g/cm<sup>3</sup>, and  $g = 9.81$  m/s<sup>2</sup>. Plugging these values into the equation and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa.)

**Equation:**

$$101,325 \text{ N/m}^2 = 101,325 \frac{\text{kg}\cdot\text{m/s}^2}{\text{m}^2} = 101,325 \frac{\text{kg}}{\text{m}\cdot\text{s}^2}$$

**Equation:**

$$p = \left( 760 \text{ mm} \times \frac{1 \text{ m}}{1000 \text{ mm}} \right) \times \left( \frac{13.6 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} \right) \times \left( \frac{9.81 \text{ m}}{1 \text{ s}^2} \right)$$

**Equation:**

$$= (0.760 \text{ m}) (13,600 \text{ kg/m}^3) (9.81 \text{ m/s}^2) = 1.01 \times 10^5 \text{ kg/ms}^2 = 1.01 \times 10^5 \text{ N/m}^2$$

**Equation:**

$$= 1.01 \times 10^5 \text{ Pa}$$

**Check Your Learning**

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm<sup>3</sup>.

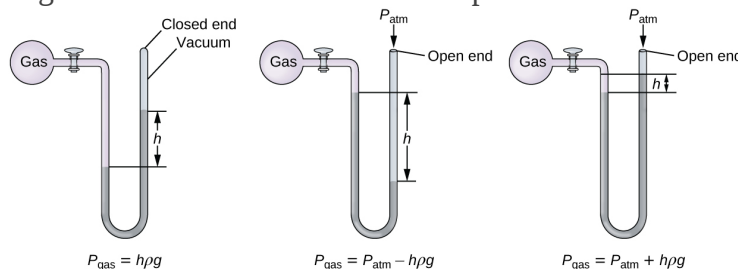
**Note:****Answer:**

10.3 m

A **manometer** is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube ( $h$  in the diagram) is proportional to the pressure of the gas in the container. An open-end



manometer ([link](#)) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.



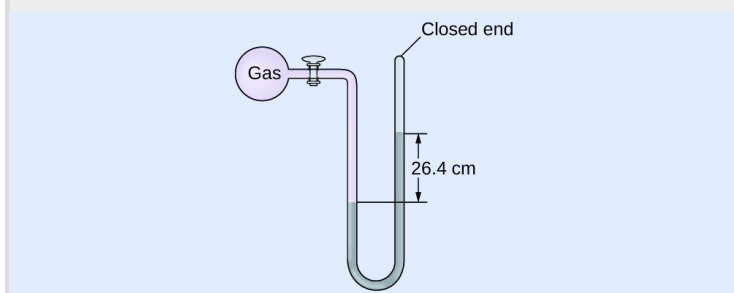
A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels ( $h$ ) is a measure of the pressure. Mercury is usually used because of its large density.

### Example:

#### Calculation of Pressure Using a Closed-End Manometer

The pressure of a sample of gas is measured with a closed-end manometer, as shown to the right. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar



#### Solution

The pressure of the gas is equal to a column of mercury of height 26.4 cm. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 26.4 cm Hg, or mercury.) We could use the equation  $p = h\rho g$  as in [link](#), but it is simpler to just convert between units using [link](#).

$$(a) \ 26.4 \text{ cm Hg} \times \frac{10 \text{ mm Hg}}{1 \text{ cm Hg}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 264 \text{ torr}$$

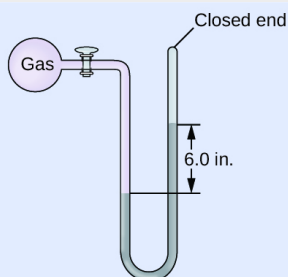
$$(b) \ 264 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} = 35,200 \text{ Pa}$$

$$(c) \ 35,200 \text{ Pa} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} = 0.352 \text{ bar}$$

#### Check Your Learning

The pressure of a sample of gas is measured with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar



**Note:**

**Answer:**

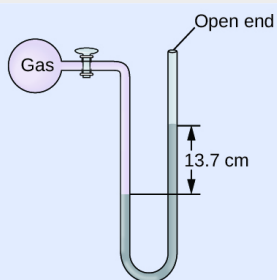
(a) ~150 torr; (b) ~20,000 Pa; (c) ~0.20 bar

**Example:**

**Calculation of Pressure Using an Open-End Manometer**

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



**Solution**

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

(a) In mm Hg, this is:  $137 \text{ mm Hg} + 760 \text{ mm Hg} = 897 \text{ mm Hg}$

(b)  $897 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.18 \text{ atm}$

(c)  $1.18 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 1.20 \times 10^2 \text{ kPa}$

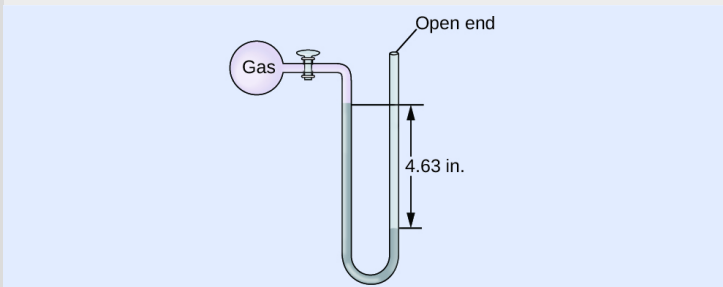
### Check Your Learning

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown to the right. Determine the pressure of the gas in:

(a) mm Hg

(b) atm

(c) kPa



### Note:

#### Answer:

(a) 642 mm Hg; (b) 0.845 atm; (c) 85.6 kPa

### Note:

#### Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = “pulse”). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded ([link](#)). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff’s pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart’s ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the

cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).

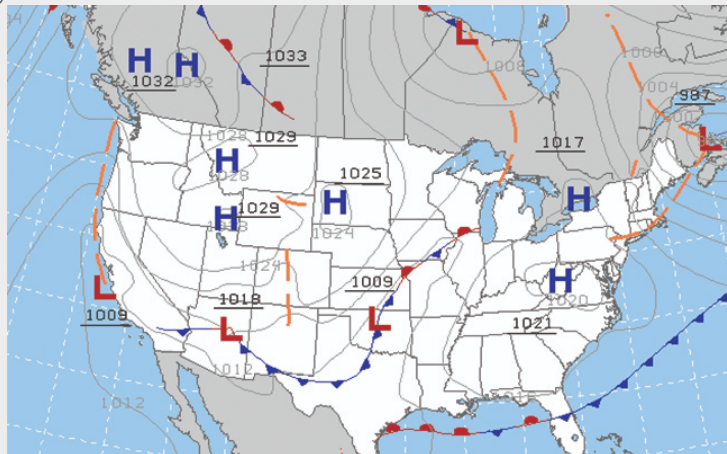


(a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer.  
(b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

### **Note:**

#### **Meteorology, Climatology, and Atmospheric Science**

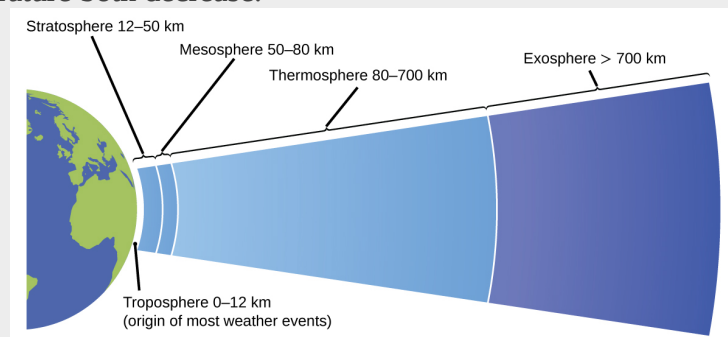
Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts ([link](#)) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.



Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions.

The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events. The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in [\[link\]](#): the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.



Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

## Key Concepts and Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

## Key Equations

$$P = \frac{F}{A}$$

$$p = h\rho g$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Why are sharp knives more effective than dull knives? (Hint: Think about the definition of pressure.)

---

#### Solution:

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

### Exercise:

#### Problem:

Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?

### Exercise:

#### Problem:

Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

---

#### Solution:

Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

**Exercise:****Problem:**

A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.

**Exercise:****Problem:**

A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

---

**Solution:**

0.809 atm; 82.0 kPa

**Exercise:****Problem:**

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?

**Exercise:****Problem:**

Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

---

**Solution:**

$2.2 \times 10^2$  kPa

**Exercise:****Problem:**

During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?

**Exercise:****Problem:**

The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

---

**Solution:**

Earth:  $14.7 \text{ lb in}^{-2}$ ; Venus:  $1.30 \times 10^3 \text{ lb in}^{-2}$

**Exercise:**

**Problem:**

A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?

**Exercise:**

**Problem:**

Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in. Hg, 1013.9 mbar.

- (a) What was the pressure in kPa?
- (b) The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.

---

**Solution:**

- (a) 101.5 kPa; (b) 51 torr drop

**Exercise:**

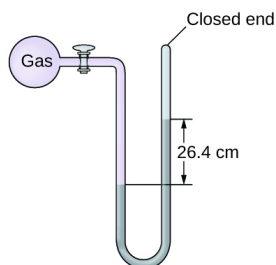
**Problem:** Why is it necessary to use a nonvolatile liquid in a barometer or manometer?

**Exercise:**

**Problem:**

The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar





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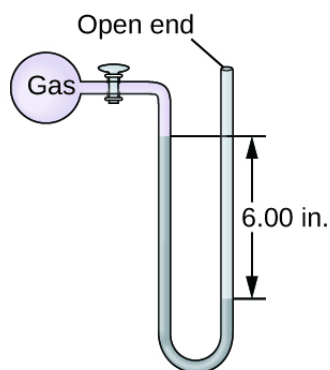
**Solution:**

(a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar

**Exercise:****Problem:**

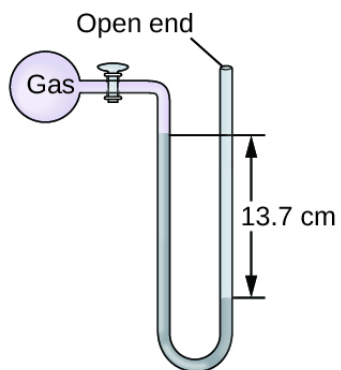
The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar

**Exercise:****Problem:**

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



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**Solution:**

(a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa

**Exercise:**

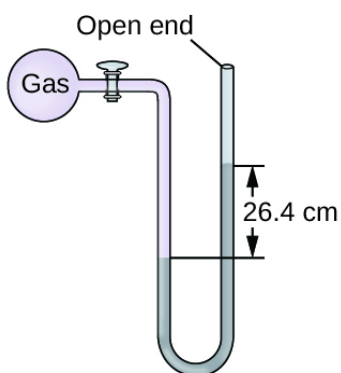
**Problem:**

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:

(a) mm Hg

(b) atm

(c) kPa



**Exercise:**

**Problem:**

How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers?

---

**Solution:**

With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since  $P_{\text{gas}} = P_{\text{atm}} + P_{\text{vol liquid}}$ .

**Glossary**

atmosphere (atm)

unit of pressure; 1 atm = 101,325 Pa

bar

(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer

device used to measure atmospheric pressure

hydrostatic pressure

pressure exerted by a fluid due to gravity

manometer

device used to measure the pressure of a gas trapped in a container

pascal (Pa)

SI unit of pressure; 1 Pa = 1 N/m<sup>2</sup>

pounds per square inch (psi)

unit of pressure common in the US

pressure

force exerted per unit area

torr

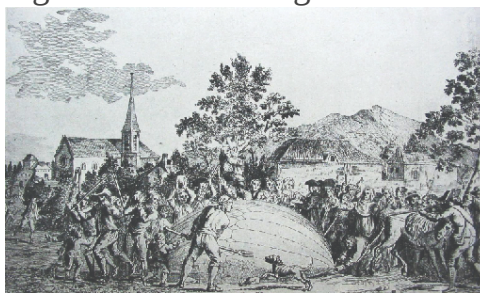
unit of pressure; 1 torr =  $\frac{1}{760}$  atm

## Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

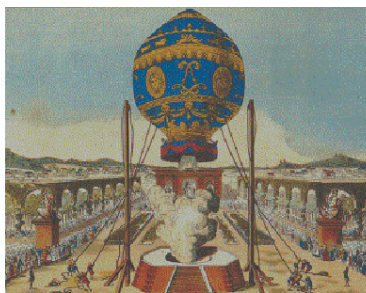
By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly ([\[link\]](#)), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



(a)



(b)



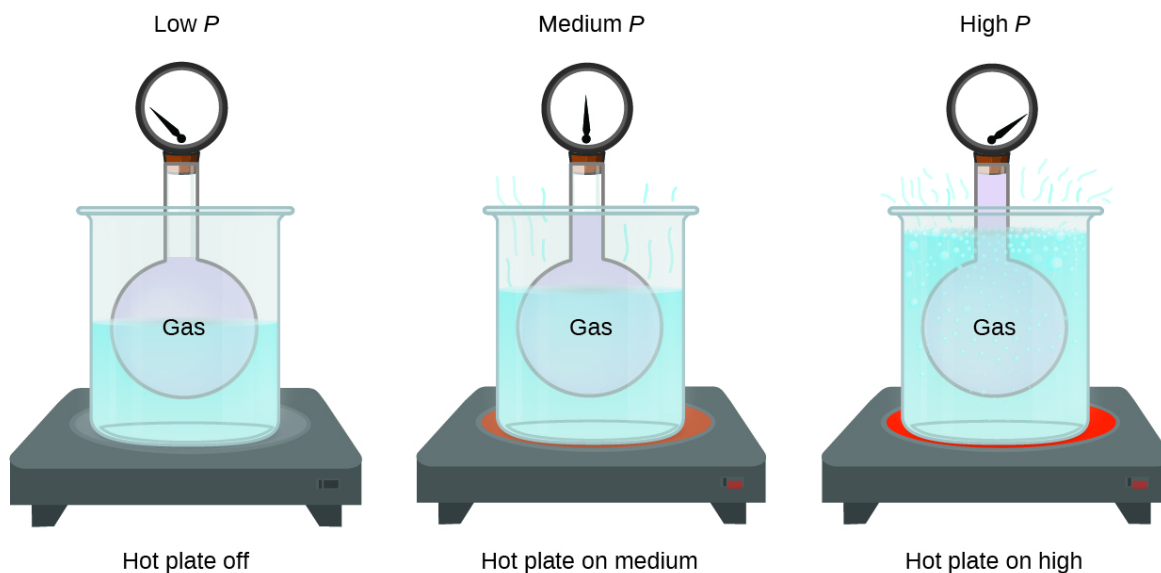
(c)

In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

## Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is

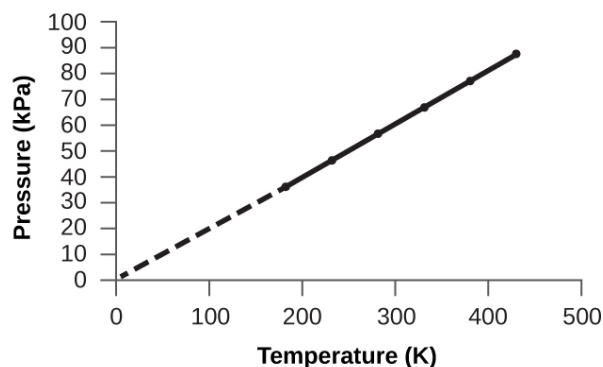
rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter ([\[link\]](#)) and the pressure increases.



The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in [\[link\]](#). We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then  $P$  and  $T$  are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
-100	173	36.0
-50	223	46.4
0	273	56.7
50	323	67.1
100	373	77.5
150	423	88.0



For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at  $-273^{\circ}\text{C}$ , which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the  $P$ - $T$  relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

**Equation:**

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where  $\propto$  means "is proportional to," and  $k$  is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio  $\frac{P}{T}$  is therefore constant (i.e.,  $\frac{P}{T} = k$ ). If the gas is initially in "Condition 1" (with  $P = P_1$  and  $T = T_1$ ), and then changes to "Condition 2" (with  $P = P_2$  and  $T = T_2$ ), we have that  $\frac{P_1}{T_1} = k$  and  $\frac{P_2}{T_2} = k$ , which reduces to  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ . This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe

how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

**Example:**

**Predicting Change in Pressure with Temperature**

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

(a) On the can is the warning “Store only at temperatures below 120 °F (48.8 °C). Do not incinerate.” Why?

(b) The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

**Solution**

(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons’s/Gay-Lussac’s law. Taking  $P_1$  and  $T_1$  as the initial values,  $T_2$  as the temperature where the pressure is unknown and  $P_2$  as the unknown pressure, and converting °C to K, we have:

**Equation:**

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives:  $P_2 = \frac{360 \text{ kPa} \times 323 \text{ K}}{297 \text{ K}} = 390 \text{ kPa}$

**Check Your Learning**

A sample of nitrogen,  $\text{N}_2$ , occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

**Note:**

**Answer:**

400 torr

## Volume and Temperature: Charles's Law

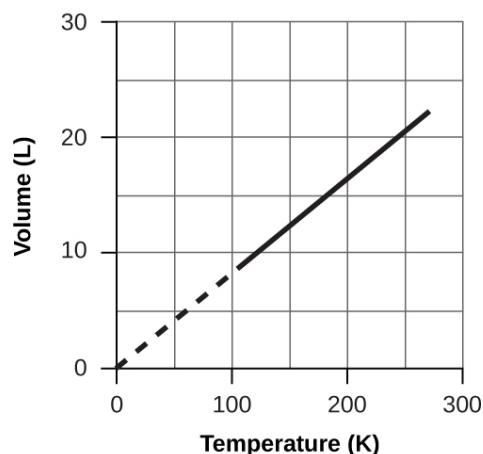
If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

### Note:

This [video](#) shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in [\[link\]](#).

Temperature (°C)	Temperature (K)	Volume (L)
-3	270	22
-23	250	21
-53	220	18
-162	111	9



The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.



The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant.*

Mathematically, this can be written as:

**Equation:**

$$V \propto T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

with  $k$  being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample,  $\frac{V}{T}$  is constant (i.e., the ratio =  $k$ ), and as seen with the  $P$ - $T$  relationship, this leads to another form of Charles's law:  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ .

**Example:**

**Predicting Change in Volume with Temperature**

A sample of carbon dioxide,  $\text{CO}_2$ , occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

**Solution**

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking  $V_1$  and  $T_1$  as the initial values,  $T_2$  as the temperature at which the volume is unknown and  $V_2$  as the unknown volume, and converting °C into K we have:

**Equation:**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives:  $V_2 = \frac{0.300 \text{ L} \times 303 \text{ K}}{283 \text{ K}} = 0.321 \text{ L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

**Check Your Learning**

A sample of oxygen,  $\text{O}_2$ , occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at −70 °C and the same pressure?

**Note:**

**Answer:**

21.6 mL

**Example:**

**Measuring Temperature with a Volume Change**

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of  $150.0 \text{ cm}^3$  when immersed in a mixture of ice and water ( $0.00^\circ\text{C}$ ). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is  $131.7 \text{ cm}^3$ . Find the temperature of boiling ammonia on the kelvin and Celsius scales.

**Solution**

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking  $V_1$  and  $T_1$  as the initial values,  $T_2$  as the temperature at which the volume is unknown and  $V_2$  as the unknown volume, and converting  $^\circ\text{C}$  into K we have:

**Equation:**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

Rearrangement gives  $T_2 = \frac{131.7 \text{ cm}^3 \times 273.15 \text{ K}}{150.0 \text{ cm}^3} = 239.8 \text{ K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is  $-33.4^\circ\text{C}$ .

**Check Your Learning**

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

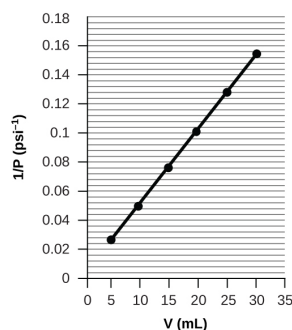
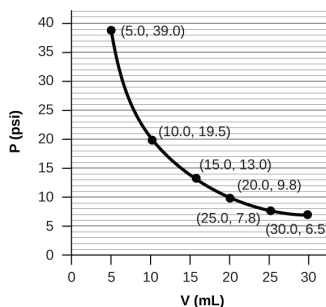
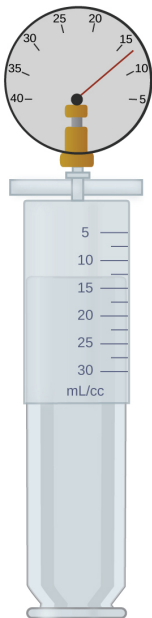
**Note:**

**Answer:**

635 mL

## Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in [\[link\]](#).



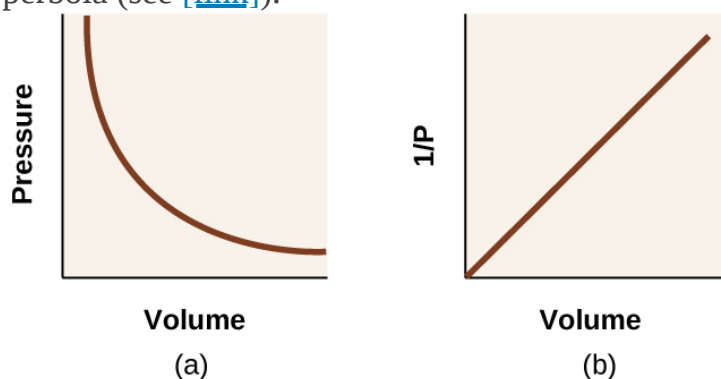
When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since  $P$  and  $V$  are inversely proportional, a graph of  $\frac{1}{P}$  vs.  $V$  is linear.

Unlike the  $P$ - $T$  and  $V$ - $T$  relationships, pressure and volume are not directly proportional to each other. Instead,  $P$  and  $V$  exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

**Equation:**

$$P \propto 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1 V_1 = P_2 V_2$$

with  $k$  being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure ( $\frac{1}{P}$ ) versus the volume ( $V$ ), or the inverse of volume ( $\frac{1}{V}$ ) versus the pressure ( $P$ ). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to “linearize” their data. If we plot  $P$  versus  $V$ , we obtain a hyperbola (see [\[link\]](#)).



The relationship between pressure and volume is inversely proportional. (a) The graph of  $P$  vs.  $V$  is a hyperbola, whereas (b) the graph of  $\left(\frac{1}{P}\right)$  vs.  $V$  is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

**Example:****Volume of a Gas Sample**

The sample of gas in [\[link\]](#) has a volume of 15.0 mL at a pressure of 13.0 psi.

Determine the pressure of the gas at a volume of 7.5 mL, using:

(a) the  $P$ - $V$  graph in [\[link\]](#)

(b) the  $\frac{1}{P}$  vs.  $V$  graph in [\[link\]](#)

(c) the Boyle's law equation

Comment on the likely accuracy of each method.

**Solution**

(a) Estimating from the  $P$ - $V$  graph gives a value for  $P$  somewhere around 27 psi.

(b) Estimating from the  $\frac{1}{P}$  versus  $V$  graph give a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume ( $PV$ ) for a given sample of gas at a constant temperature is always equal to the same value.

Therefore we have  $P_1V_1 = k$  and  $P_2V_2 = k$  which means that  $P_1V_1 = P_2V_2$ .

Using  $P_1$  and  $V_1$  as the known values 13.0 psi and 15.0 mL,  $P_2$  as the pressure at which the volume is unknown, and  $V_2$  as the unknown volume, we have:

**Equation:**

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

**Equation:**

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ psi}$$

It was more difficult to estimate well from the  $P$ - $V$  graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

**Check Your Learning**

The sample of gas in [\[link\]](#) has a volume of 30.0 mL at a pressure of 6.5 psi.

Determine the volume of the gas at a pressure of 11.0 psi, using:

(a) the  $P$ - $V$  graph in [\[link\]](#)

(b) the  $\frac{1}{P}$  vs.  $V$  graph in [\[link\]](#)

(c) the Boyle's law equation

Comment on the likely accuracy of each method.

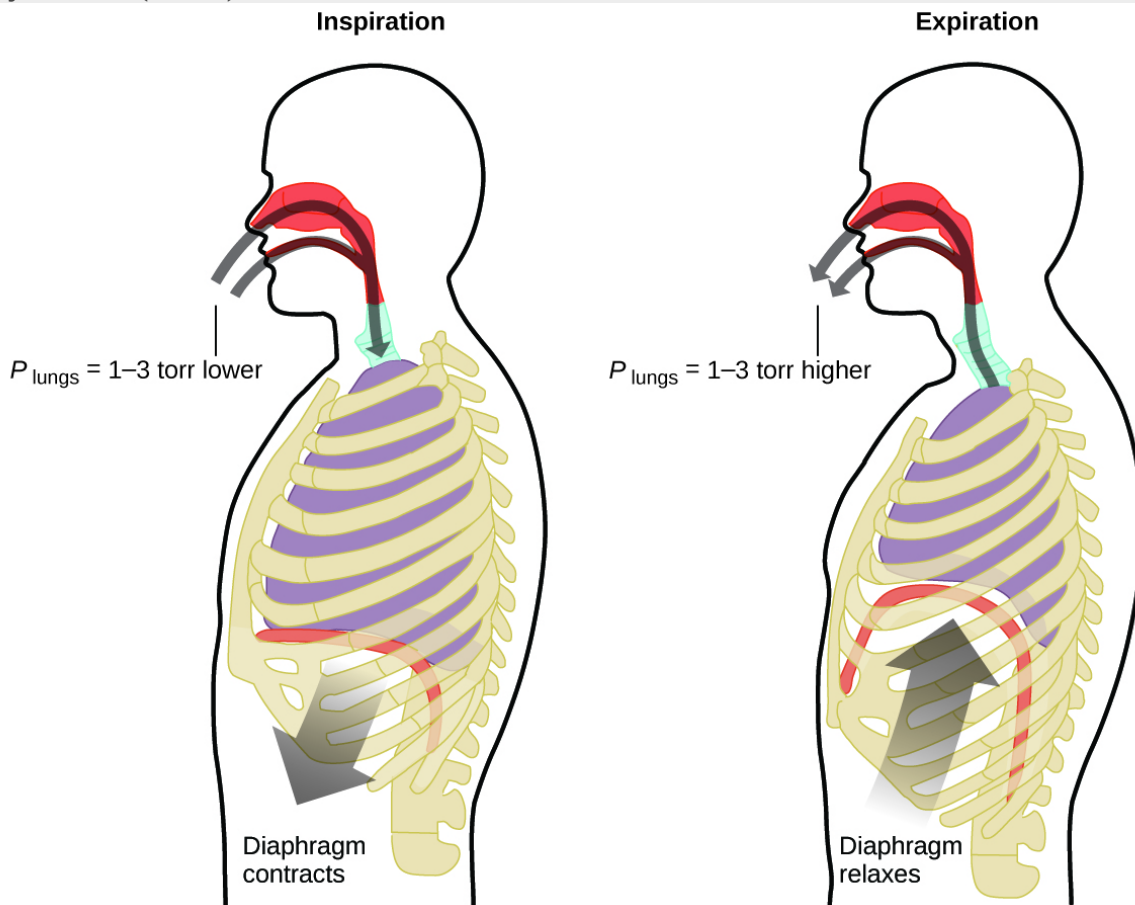
**Note:**

**Answer:**

(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the  $P$ - $V$  graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

**Note:****Breathing and Boyle's Law**

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life ([\[link\]](#)).



Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be

drawn into and forced out of your lungs.

## Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume ( $V$ ) and number of moles ( $n$ ) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

**Equation:**

$$V \propto n \quad \text{or} \quad V = k \times n \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as  $P$  versus  $n$ , and  $n$  versus  $T$ .

### Note:

Visit this [interactive PhET simulation](#) to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

## The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law:  $PV = \text{constant}$  at constant  $T$  and  $n$
- Amontons's law:  $\frac{P}{T} = \text{constant}$  at constant  $V$  and  $n$
- Charles's law:  $\frac{V}{T} = \text{constant}$  at constant  $P$  and  $n$
- Avogadro's law:  $\frac{V}{n} = \text{constant}$  at constant  $P$  and  $T$

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

**Equation:**

$$PV = nRT$$

where  $P$  is the pressure of a gas,  $V$  is its volume,  $n$  is the number of moles of the gas,  $T$  is its temperature on the kelvin scale, and  $R$  is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being  $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$  and  $8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1}$ .

Gases whose properties of  $P$ ,  $V$ , and  $T$  are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant  $R$  and the variable properties  $P$ ,  $V$ ,  $n$ , and  $T$ . Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

**Example:**

**Using the Ideal Gas Law**

Methane,  $\text{CH}_4$ , is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of  $\text{CH}_4$ . What is the volume of this much methane at  $25^\circ\text{C}$  and 745 torr?

**Solution**

We must rearrange  $PV = nRT$  to solve for  $V$ :  $V = \frac{nRT}{P}$

If we choose to use  $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ , then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the “right” units:

**Equation:**



$$n = 655 \text{ g CH}_4 \times \frac{1 \text{ mol}}{16.043 \text{ g CH}_4} = 40.8 \text{ mol}$$

**Equation:**

$$T = 25^\circ\text{C} + 273 = 298 \text{ K}$$

**Equation:**

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

**Equation:**

$$V = \frac{nRT}{P} = \frac{(40.8 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

### Check Your Learning

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

**Note:**

**Answer:**

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained:  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$  using units of atm, L, and K. Both sets of conditions are equal to the product of  $n \times R$  (where  $n$  = the number of moles of the gas and  $R$  is the ideal gas law constant).

**Example:**

### Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm ([link](#)). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting 1 represent the air in the scuba tank and 2 represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

**Equation:**

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \longrightarrow \frac{(153 \text{ atm})(13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm})(V_2)}{(310 \text{ K})}$$

Solving for  $V_2$ :

**Equation:**

$$V_2 = \frac{(153 \text{ atm})(13.2 \text{ L})(310 \text{ K})}{(300 \text{ K})(3.13 \text{ atm})} = 667 \text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good “ballpark” estimate.)

**Check Your Learning**

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

**Note:**

**Answer:**

0.193 L

**Note:**

**The Interdependence between Ocean Depth and Pressure in Scuba Diving**

Whether scuba diving at the Great Barrier Reef in Australia (shown in [\[link\]](#)) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle’s law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

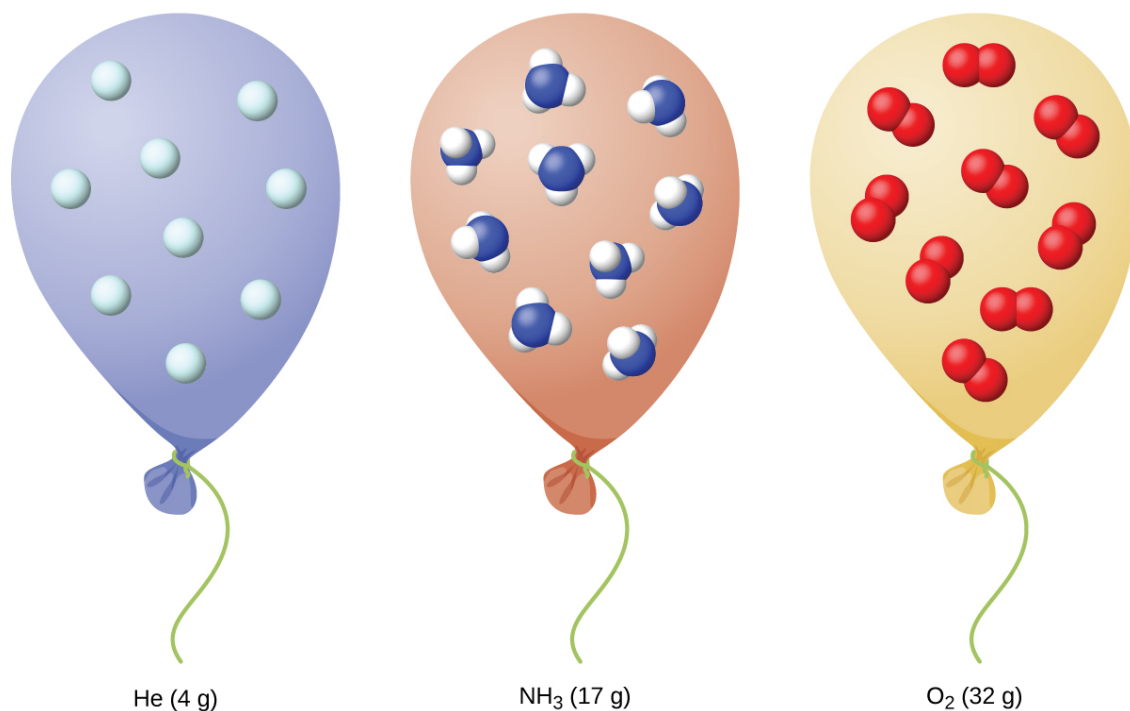
## Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature.

Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa).

[\[footnote\]](#) At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** ([\[link\]](#)).

The IUPAC definition of standard pressure was changed from 1 atm to 1 bar (100 kPa) in 1982, but the prior definition remains in use by many literature resources and will be used in this text.



Regardless of its chemical identity, one mole of gas behaving ideally occupies a volume of  $\sim 22.4$  L at STP.

## Key Concepts and Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law,  $PV = nRT$ , where  $P$  is the pressure of the gas,  $V$  is its volume,  $n$  is the number of moles of the gas,  $T$  is its kelvin temperature, and  $R$  is the ideal (universal) gas constant.

## Key Equations

$$PV = nRT$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

### Exercise:

#### Problem:

Explain how the volume of the bubbles exhausted by a scuba diver ([link](#)) change as they rise to the surface, assuming that they remain intact.

---

#### Solution:

As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

### Exercise:

#### Problem:

One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must be equal?

### Exercise:

#### Problem:

An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas." (a) What is the meaning of the term "directly proportional?" (b) What are the "other things" that must be equal?

---

#### Solution:

(a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure

### Exercise:

**Problem:**

How would the graph in [\[link\]](#) change if the number of moles of gas in the sample used to determine the curve were doubled?

**Exercise:****Problem:**

How would the graph in [\[link\]](#) change if the number of moles of gas in the sample used to determine the curve were doubled?

---

**Solution:**

The curve would be farther to the right and higher up, but the same basic shape.

**Exercise:****Problem:**

In addition to the data found in [\[link\]](#), what other information do we need to find the mass of the sample of air used to determine the graph?

**Exercise:****Problem:**

Determine the volume of 1 mol of  $\text{CH}_4$  gas at 150 K and 1 atm, using [\[link\]](#).

---

**Solution:**

About 12.5 L

**Exercise:****Problem:**

Determine the pressure of the gas in the syringe shown in [\[link\]](#) when its volume is 12.5 mL, using:

- (a) the appropriate graph
- (b) Boyle's law

**Exercise:**

**Problem:**

A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire ( $T = 475\text{ °C}$ ), what will be the pressure in the hot can?

---

**Solution:**

$$3.40 \times 10^3 \text{ torr}$$

**Exercise:****Problem:**

What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

**Exercise:****Problem:**

A 2.50-L volume of hydrogen measured at  $-196\text{ °C}$  is warmed to  $100\text{ °C}$ . Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

---

**Solution:**

$$12.1 \text{ L}$$

**Exercise:****Problem:**

A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

**Exercise:****Problem:**

A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of  $25\text{ °C}$  at ground level. What is the volume of the balloon under these conditions?





---

**Solution:**

217 L

**Exercise:**

**Problem:**

The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?

**Exercise:**

**Problem:**

How many moles of gaseous boron trifluoride,  $\text{BF}_3$ , are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of  $\text{BF}_3$ ?

---

**Solution:**

$8.190 \times 10^{-2}$  mol; 5.553 g

**Exercise:**

**Problem:**

Iodine,  $\text{I}_2$ , is a solid at room temperature but sublimates (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of  $\text{I}_2$  vapor at a pressure of 0.462 atm?

**Exercise:**

**Problem:** How many grams of gas are present in each of the following cases?

- (a) 0.100 L of CO<sub>2</sub> at 307 torr and 26 °C
- (b) 8.75 L of C<sub>2</sub>H<sub>4</sub>, at 378.3 kPa and 483 K
- (c) 221 mL of Ar at 0.23 torr and −54 °C

---

**Solution:**

(a)  $7.24 \times 10^{-2}$  g; (b) 23.1 g; (c)  $1.5 \times 10^{-4}$  g

**Exercise:**

**Problem:**

A high altitude balloon is filled with  $1.41 \times 10^4$  L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is −48 °C and the pressure is 63.1 torr?

**Exercise:**

**Problem:**

A cylinder of medical oxygen has a volume of 35.4 L, and contains O<sub>2</sub> at a pressure of 151 atm and a temperature of 25 °C. What volume of O<sub>2</sub> does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

---

**Solution:**

5561 L

**Exercise:**

**Problem:**

A large scuba tank ([link](#)) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20 °C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20 °C?

**Exercise:**

**Problem:**

A 20.0-L cylinder containing 11.34 kg of butane,  $\text{C}_4\text{H}_{10}$ , was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

---

**Solution:**

46.4 g

**Exercise:****Problem:**

While resting, the average 70-kg human male consumes 14 L of pure  $\text{O}_2$  per hour at 25 °C and 100 kPa. How many moles of  $\text{O}_2$  are consumed by a 70 kg man while resting for 1.0 h?

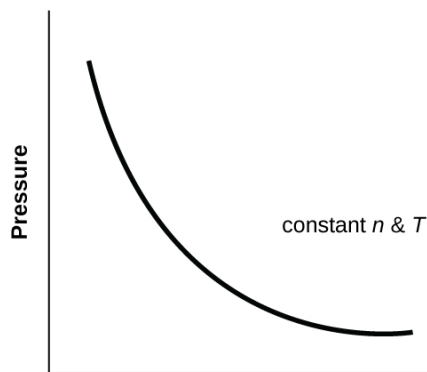
**Exercise:****Problem:**

For a given amount of gas showing ideal behavior, draw labeled graphs of:

- (a) the variation of  $P$  with  $V$
  - (b) the variation of  $V$  with  $T$
  - (c) the variation of  $P$  with  $T$
  - (d) the variation of  $\frac{1}{P}$  with  $V$
- 

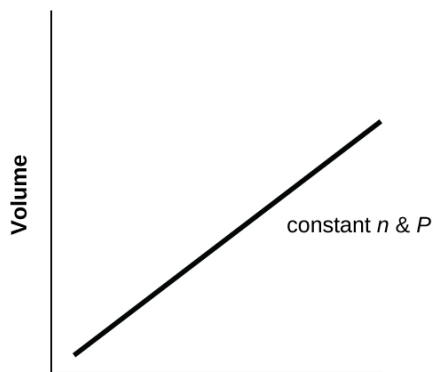
**Solution:**

For a gas exhibiting ideal behavior:



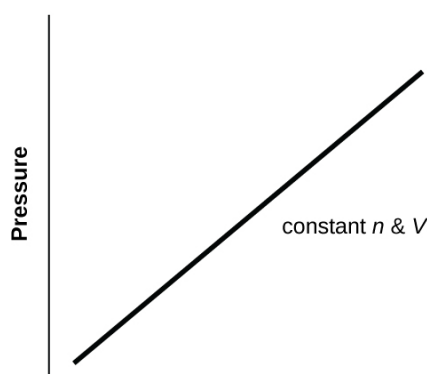
Volume

(a)



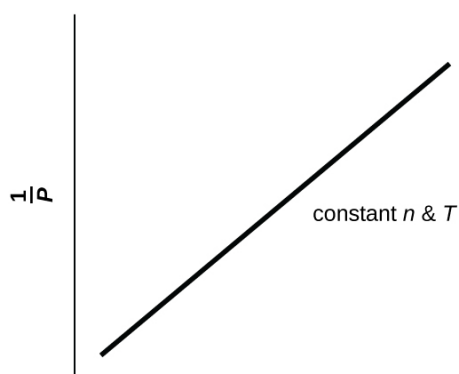
Temperature

(b)



Temperature

(c)



Volume

(d)

### Exercise:

#### Problem:

A liter of methane gas,  $\text{CH}_4$ , at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas,  $\text{H}_2$ , at STP. Using Avogadro's law as a starting point, explain why.

### Exercise:

#### Problem:

The effect of chlorofluorocarbons (such as  $\text{CCl}_2\text{F}_2$ ) on the depletion of the ozone layer is well known. The use of substitutes, such as  $\text{CH}_3\text{CH}_2\text{F}(g)$ , for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

(a)  $\text{CCl}_2\text{F}_2(g)$

(b)  $\text{CH}_3\text{CH}_2\text{F}(g)$

---

**Solution:**

(a) 1.85 L  $\text{CCl}_2\text{F}_2$ ; (b) 4.66 L  $\text{CH}_3\text{CH}_2\text{F}$

**Exercise:**

**Problem:**

As 1 g of the radioactive element radium decays over 1 year, it produces  $1.16 \times 10^{18}$  alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

**Exercise:**

**Problem:**

A balloon with a volume of 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

---

**Solution:**

0.644 atm

**Exercise:**

**Problem:**

If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

**Exercise:**

**Problem:**

If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

---

**Solution:**

The pressure decreases by a factor of 3.

**Glossary**

absolute zero

temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law

(also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Avogadro's law

volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Boyle's law

volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law

volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

ideal gas

hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant ( $R$ )

constant derived from the ideal gas equation  $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$  or  $8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$

ideal gas law

relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)

273.15 K (0 °C) and 1 atm (101.325 kPa)

standard molar volume

volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

## Stoichiometry of Gaseous Substances, Mixtures, and Reactions

By the end of this section, you will be able to:

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton's law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the “father of modern chemistry,” changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, “It took the mob only a moment to remove his head; a century will not suffice to reproduce it.”<sup>[footnote]</sup> “Quotations by Joseph-Louis Lagrange,” last modified February 2006, accessed February 10, 2015, <http://www-history.mcs.st-andrews.ac.uk/Quotations/Lagrange.html>

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask “How much?” The essential property involved in such use of stoichiometry is the amount of substance, typically measured in moles ( $n$ ). For gases, molar amount can be derived from convenient experimental measurements of pressure, temperature, and volume. Therefore, these measurements are useful in assessing the stoichiometry of pure gases, gas mixtures, and chemical reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

### Gas Density and Molar Mass

The ideal gas law described previously in this chapter relates the properties of pressure  $P$ , volume  $V$ , temperature  $T$ , and molar amount  $n$ . This law is universal, relating these properties in identical fashion regardless of the chemical identity of the gas:

**Equation:**

$$PV = nRT$$

The density  $d$  of a gas, on the other hand, is determined by its identity. As described in another chapter of this text, the density of a substance is a characteristic property that may be used to identify the substance.

**Equation:**

$$d = \frac{m}{V}$$

Rearranging the ideal gas equation to isolate  $V$  and substituting into the density equation yields

**Equation:**

$$d = \frac{mP}{nRT} = \left(\frac{m}{n}\right) \frac{P}{RT}$$

The ratio  $m/n$  is the definition of molar mass,  $\mathcal{M}$ :

**Equation:**

$$\mathcal{M} = \frac{m}{n}$$

The density equation can then be written

**Equation:**

$$d = \frac{\mathcal{M}P}{RT}$$

This relation may be used for calculating the densities of gases of known identities at specified values of pressure and temperature as demonstrated in [\[link\]](#).

**Example:**

**Measuring Gas Density**

What is the density of molecular nitrogen gas at STP?

**Solution**

The molar mass of molecular nitrogen, N<sub>2</sub>, is 28.01 g/mol. Substituting this value along with standard temperature and pressure into the gas density equation yields

**Equation:**

$$d = \frac{\mathcal{M}P}{RT} = \frac{(28.01 \text{ g/mol})(1.00 \text{ atm})}{(0.0821 \text{ L atm mol}^{-1}\text{K}^{-1})(273 \text{ K})} = 1.25 \text{ g / L}$$

**Check Your Learning**

What is the density of molecular hydrogen gas at 17.0 °C and a pressure of 760 torr?

**Note:**

**Answer:**

d = 0.0847 g/L

When the identity of a gas is unknown, measurements of the mass, pressure, volume, and temperature of a sample can be used to calculate the molar mass of the gas (a useful property for identification purposes). Combining the ideal gas equation

**Equation:**

$$PV = nRT$$

and the definition of molarity

**Equation:**

$$\mathcal{M} = \frac{m}{n}$$

yields the following equation:

**Equation:**

$$\mathcal{M} = \frac{mRT}{PV}$$



Determining the molar mass of a gas via this approach is demonstrated in [\[link\]](#).

**Example:**

**Determining the Molecular Formula of a Gas from its Molar Mass and Empirical Formula**

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

**Solution**

First determine the empirical formula of the gas. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

**Equation:**

$$85.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.136 \text{ mol C} \quad \frac{7.136}{7.136} = 1.00 \text{ mol C}$$

**Equation:**

$$14.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 14.158 \text{ mol H} \quad \frac{14.158}{7.136} = 1.98 \text{ mol H}$$

Empirical formula is CH<sub>2</sub> [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the provided values for mass, pressure, temperature and volume to compute the molar mass of the gas:

**Equation:**

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(1.56 \text{ g})(0.0821 \text{ L atm mol}^{-1}\text{K}^{-1})(323 \text{ K})}{(0.984 \text{ atm})(1.00 \text{ L})} = 42.0 \text{ g/mol}$$

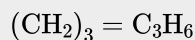
Comparing the molar mass to the empirical formula mass shows how many empirical formula units make up a molecule:

**Equation:**

$$\frac{\mathcal{M}}{EM} = \frac{42.0 \text{ g/mol}}{14.0 \text{ g/mol}} = 3$$

The molecular formula is thus derived from the empirical formula by multiplying each of its subscripts by three:

**Equation:**



**Check Your Learning**

Acetylene, a fuel used welding torches, is composed of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

**Note:**

**Answer:**

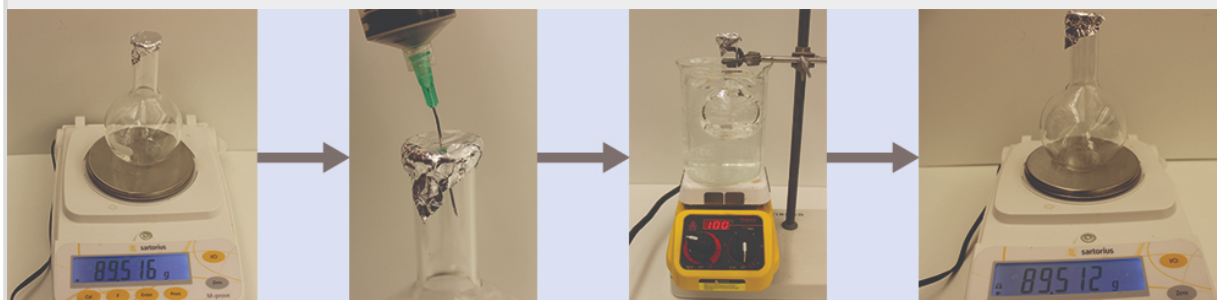
Empirical formula, CH; Molecular formula, C<sub>2</sub>H<sub>2</sub>

**Example:**

**Determining the Molar Mass of a Volatile Liquid**

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see [\[link\]](#))



When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At  $t_l \rightarrow g$ , the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm<sup>3</sup> at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

**Solution**

Since  $\mathcal{M} = \frac{m}{n}$  and  $n = \frac{PV}{RT}$ , substituting and rearranging gives  $\mathcal{M} = \frac{mRT}{PV}$ , then

**Equation:**

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494 \text{ g}) \times 0.08206 \text{ L}\cdot\text{atm/mol K} \times 372.8 \text{ K}}{0.976 \text{ atm} \times 0.129 \text{ L}} = 120 \text{ g/mol.}$$

**Check Your Learning**

A sample of phosphorus that weighs  $3.243 \times 10^{-2}$  g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

**Note:**

**Answer:**

124 g/mol P<sub>4</sub>

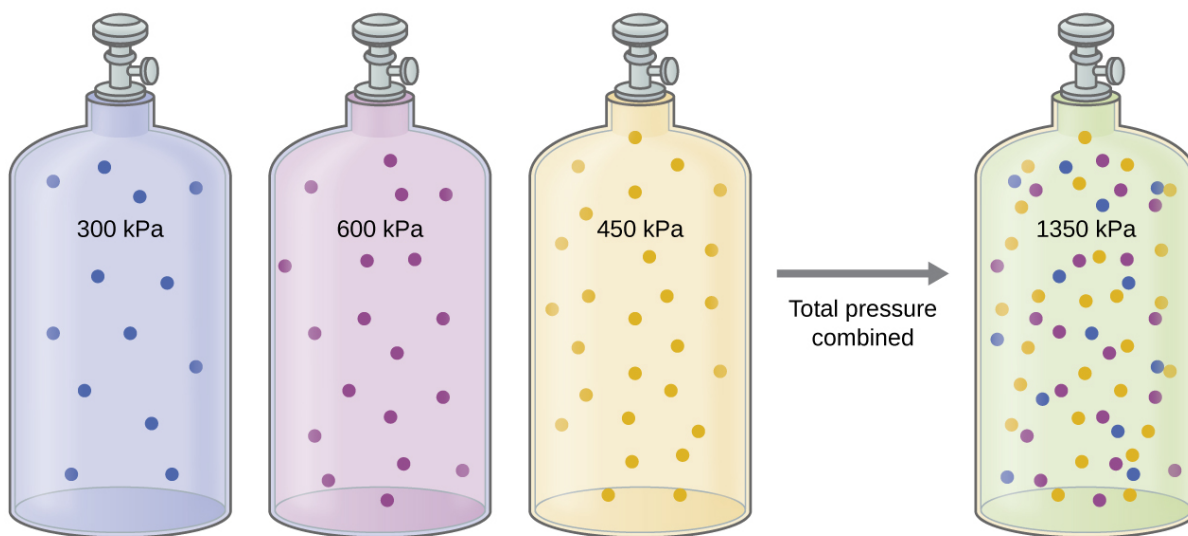
## The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container ([link](#)). The pressure exerted by each individual gas in a mixture is called its **partial pressure**. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

**Equation:**

$$P_{Total} = P_A + P_B + P_C + \dots = \sum_i P_i$$

In the equation  $P_{Total}$  is the total pressure of a mixture of gases,  $P_A$  is the partial pressure of gas A;  $P_B$  is the partial pressure of gas B;  $P_C$  is the partial pressure of gas C; and so on.



If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction (X)**, a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

**Equation:**

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where  $P_A$ ,  $X_A$ , and  $n_A$  are the partial pressure, mole fraction, and number of moles of gas A, respectively, and  $n_{Total}$  is the number of moles of all components in the mixture.

**Example:**

**The Pressure of a Mixture of Gases**

A 10.0-L vessel contains  $2.50 \times 10^{-3}$  mol of  $H_2$ ,  $1.00 \times 10^{-3}$  mol of He, and  $3.00 \times 10^{-4}$  mol of Ne at 35 °C.

(a) What are the partial pressures of each of the gases?

(b) What is the total pressure in atmospheres?

**Solution**

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using  $P = \frac{nRT}{V}$ :

**Equation:**

$$P_{H_2} = \frac{(2.50 \times 10^{-3} \text{ mol}) (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (308 \text{ K})}{10.0 \text{ L}} = 6.32 \times 10^{-3} \text{ atm}$$

**Equation:**

$$P_{He} = \frac{(1.00 \times 10^{-3} \text{ mol}) (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (308 \text{ K})}{10.0 \text{ L}} = 2.53 \times 10^{-3} \text{ atm}$$

**Equation:**

$$P_{Ne} = \frac{(3.00 \times 10^{-4} \text{ mol}) (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (308 \text{ K})}{10.0 \text{ L}} = 7.58 \times 10^{-4} \text{ atm}$$

The total pressure is given by the sum of the partial pressures:

**Equation:**

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

**Check Your Learning**

A 5.73-L flask at 25 °C contains 0.0388 mol of  $N_2$ , 0.147 mol of CO, and 0.0803 mol of  $H_2$ . What is the total pressure in the flask in atmospheres?

**Note:**

**Answer:**

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

**Example:**

**The Pressure of a Mixture of Gases**

A gas mixture used for anesthesia contains 2.83 mol oxygen,  $O_2$ , and 8.41 mol nitrous oxide,  $N_2O$ . The total pressure of the mixture is 192 kPa.

- (a) What are the mole fractions of O<sub>2</sub> and N<sub>2</sub>O?  
(b) What are the partial pressures of O<sub>2</sub> and N<sub>2</sub>O?

**Solution**

The mole fraction is given by  $X_A = \frac{n_A}{n_{Total}}$  and the partial pressure is  $P_A = X_A \times P_{Total}$ .

For O<sub>2</sub>,

**Equation:**

$$X_{O_2} = \frac{n_{O_2}}{n_{Total}} = \frac{2.83 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.252$$

and  $P_{O_2} = X_{O_2} \times P_{Total} = 0.252 \times 192 \text{ kPa} = 48.4 \text{ kPa}$

For N<sub>2</sub>O,

**Equation:**

$$X_{N_2} = \frac{n_{N_2}}{n_{Total}} = \frac{8.41 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.748$$

and

$P_{N_2} = X_{N_2} \times P_{Total} = 0.748 \times 192 \text{ kPa} = 143.6 \text{ kPa}$

**Check Your Learning**

What is the pressure of a mixture of 0.200 g of H<sub>2</sub>, 1.00 g of N<sub>2</sub>, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

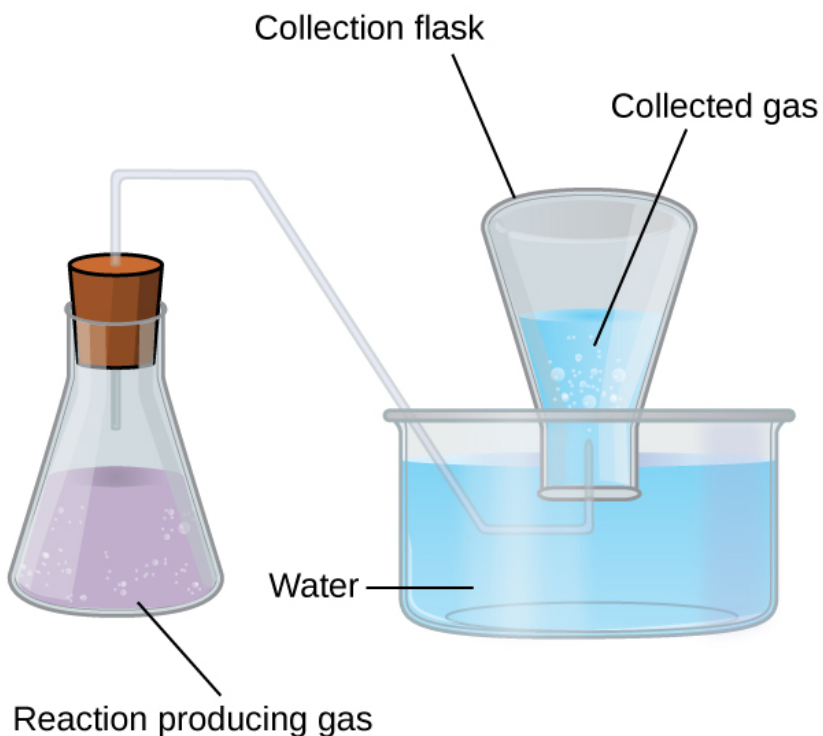
**Note:**

**Answer:**

1.87 atm

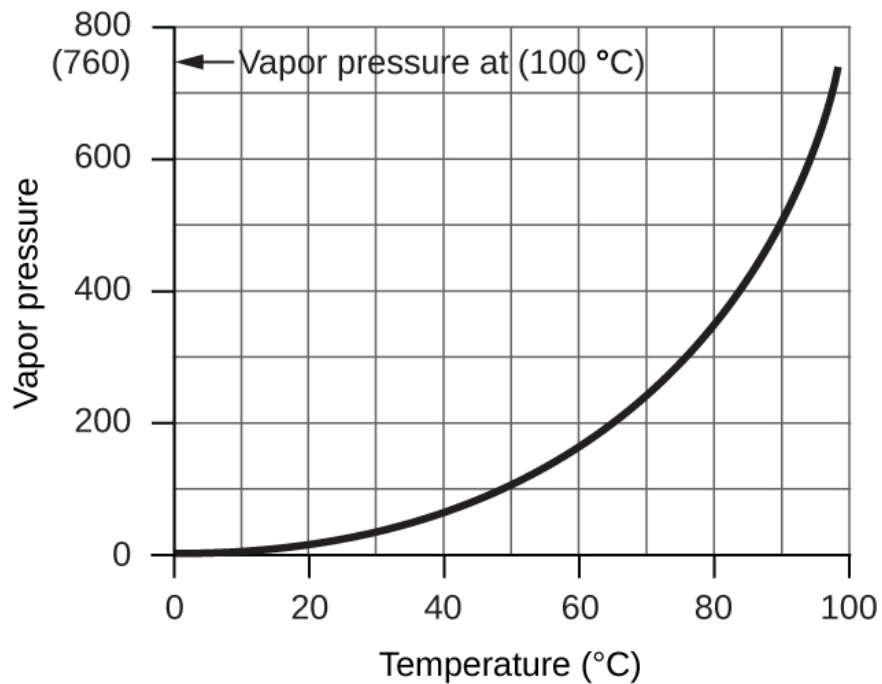
## Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle ([link](#)), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.



When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor. The **vapor pressure of water**, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature ([link](#)); more detailed information on the temperature dependence of water vapor can be found in [link](#), and vapor pressure will be discussed in more detail in the chapter on liquids.



This graph shows the vapor pressure of water at sea level as a function of temperature.

Vapor Pressure of Ice and Water in Various Temperatures at Sea Level							
Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)
−10	1.95		18	15.5		30	31.8
−5	3.0		19	16.5		35	42.2
−2	3.9		20	17.5		40	55.3
0	4.6		21	18.7		50	92.5
2	5.3		22	19.8		60	149.4
4	6.1		23	21.1		70	233.7
6	7.0		24	22.4		80	355.1
8	8.0		25	23.8		90	525.8

Vapor Pressure of Ice and Water in Various Temperatures at Sea Level							
Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)
10	9.2		26	25.2		95	633.9
12	10.5		27	26.7		99	733.2
14	12.0		28	28.3		100.0	760.0
16	13.6		29	30.0		101.0	787.6

### Example:

#### Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in [\[link\]](#), what is the partial pressure of argon?

#### Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

#### Equation:

$$P_T = P_{Ar} + P_{H_2O}$$

Rearranging this equation to solve for the pressure of argon gives:

#### Equation:

$$P_{Ar} = P_T - P_{H_2O}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr ([Appendix E](#)), so:

#### Equation:

$$P_{Ar} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

#### Check Your Learning

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

#### Note:

#### Answer:

0.583 L

## Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions.



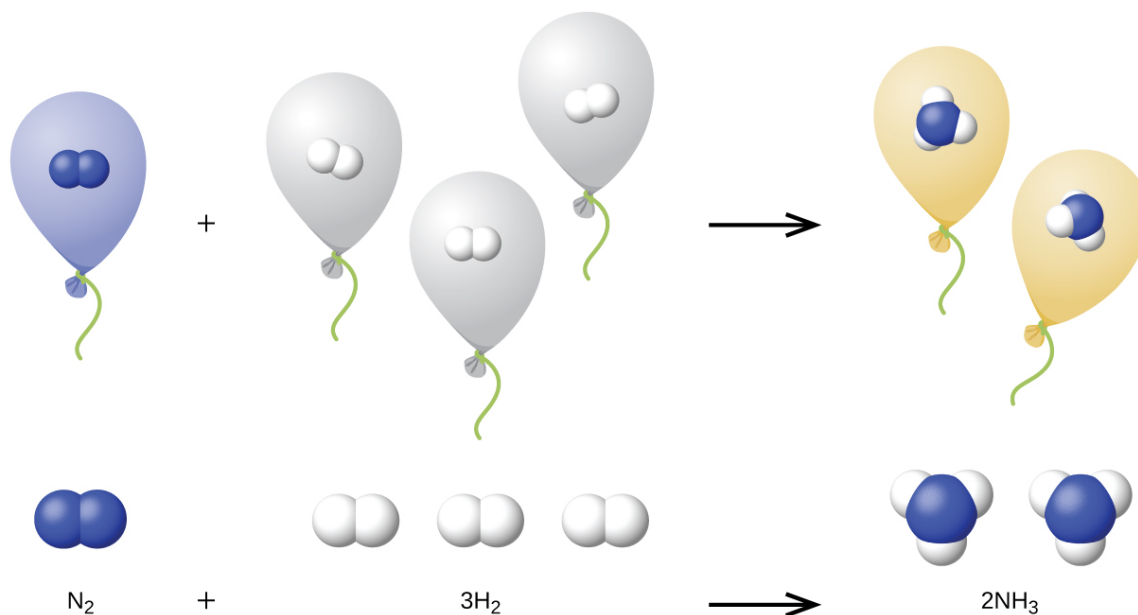
We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

### Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to  $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$ , a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in [\[link\]](#). According to Avogadro's law, equal volumes of gaseous  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ , at the same temperature and pressure, contain the same number of molecules. Because one molecule of  $\text{N}_2$  reacts with three molecules of  $\text{H}_2$  to produce two molecules of  $\text{NH}_3$ , the volume of  $\text{H}_2$  required is three times the volume of  $\text{N}_2$ , and the volume of  $\text{NH}_3$  produced is two times the volume of  $\text{N}_2$ .



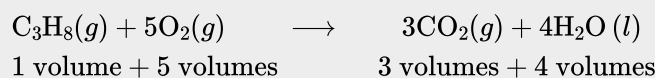
One volume of  $\text{N}_2$  combines with three volumes of  $\text{H}_2$  to form two volumes of  $\text{NH}_3$ .

**Example:****Reaction of Gases**

Propane,  $\text{C}_3\text{H}_8(g)$ , is used in gas grills to provide the heat for cooking. What volume of  $\text{O}_2(g)$  measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

**Solution**

The ratio of the volumes of  $\text{C}_3\text{H}_8$  and  $\text{O}_2$  will be equal to the ratio of their coefficients in the balanced equation for the reaction:

**Equation:**

From the equation, we see that one volume of  $\text{C}_3\text{H}_8$  will react with five volumes of  $\text{O}_2$ :

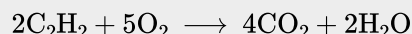
**Equation:**

$$2.7 \text{ L } \text{C}_3\text{H}_8 \times \frac{5 \text{ L } \text{O}_2}{1 \text{ L } \text{C}_3\text{H}_8} = 13.5 \text{ L } \text{O}_2$$

A volume of 13.5 L of  $\text{O}_2$  will be required to react with 2.7 L of  $\text{C}_3\text{H}_8$ .

**Check Your Learning**

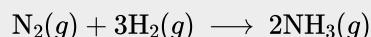
An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas,  $\text{C}_2\text{H}_2$ , at 0 °C and 1 atm. How many tanks of oxygen, each providing  $7.00 \times 10^3$  L of  $\text{O}_2$  at 0 °C and 1 atm, will be required to burn the acetylene?

**Equation:****Note:****Answer:**

3.34 tanks ( $2.34 \times 10^4$  L)

**Example:****Volumes of Reacting Gases**

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of  $\text{H}_2(g)$ , measured under the same conditions, was required to prepare this amount of ammonia by reaction with  $\text{N}_2$ ?

**Equation:****Solution**

Because equal volumes of  $\text{H}_2$  and  $\text{NH}_3$  contain equal numbers of molecules and each three molecules of  $\text{H}_2$  that react produce two molecules of  $\text{NH}_3$ , the ratio of the volumes of  $\text{H}_2$  and  $\text{NH}_3$  will be equal to 3:2. Two volumes of  $\text{NH}_3$ , in this case in units of billion  $\text{ft}^3$ , will be formed from three volumes of  $\text{H}_2$ :

**Equation:**

$$683 \text{ billion ft}^3 \text{ NH}_3 \times \frac{3 \text{ billion ft}^3 \text{ H}_2}{2 \text{ billion ft}^3 \text{ NH}_3} = 1.02 \times 10^3 \text{ billion ft}^3 \text{ H}_2$$

The manufacture of 683 billion ft<sup>3</sup> of NH<sub>3</sub> required 1020 billion ft<sup>3</sup> of H<sub>2</sub>. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

### Check Your Learning

What volume of O<sub>2</sub>(g) measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, C<sub>2</sub>H<sub>4</sub>(g), measured under the same conditions of temperature and pressure? The products are CO<sub>2</sub> and water vapor.

**Note:**

**Answer:**

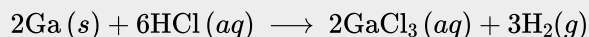
51.0 L

### Example:

#### Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

#### Equation:



#### Solution

Convert the provided mass of the limiting reactant, Ga, to moles of hydrogen produced:

#### Equation:

$$8.88 \text{ g Ga} \times \frac{1 \text{ mol Ga}}{69.723 \text{ g Ga}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Ga}} = 0.191 \text{ mol H}_2$$

Convert the provided temperature and pressure values to appropriate units (K and atm, respectively), and then use the molar amount of hydrogen gas and the ideal gas equation to calculate the volume of gas:

#### Equation:

$$V = \left( \frac{nRT}{P} \right) = \frac{0.191 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.951 \text{ atm}} = 4.94 \text{ L}$$

### Check Your Learning

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO<sub>2</sub> at 343 °C and 1.21 atm is produced by burning 1.00 kg of sulfur in excess oxygen?

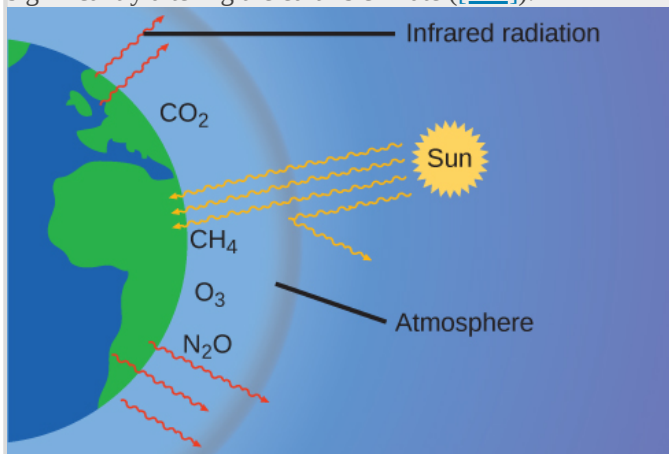
**Note:**

**Answer:**

$1.30 \times 10^3 \text{ L}$

**Note:****Greenhouse Gases and Climate Change**

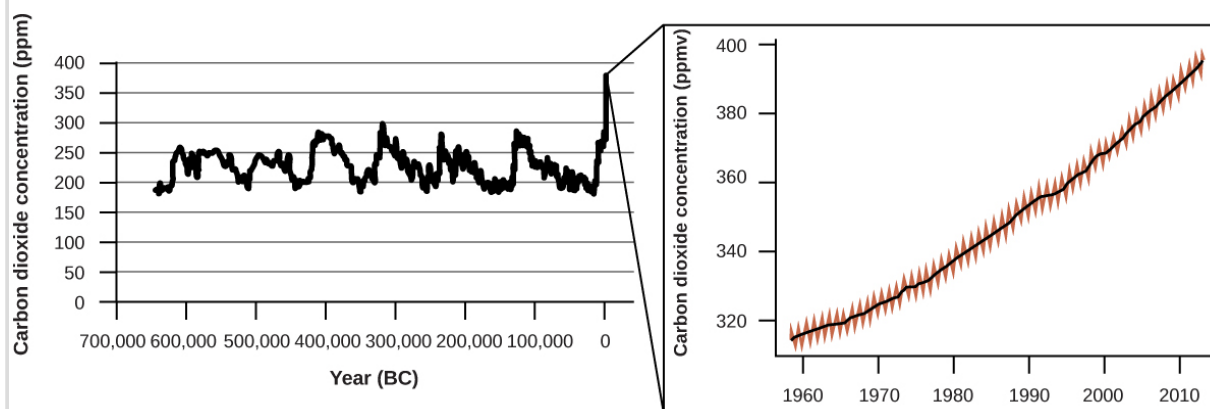
The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost  $\frac{1}{3}$  is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. Most of this IR radiation, however, is absorbed by certain atmospheric gases, effectively trapping heat within the atmosphere in a phenomenon known as the *greenhouse effect*. This effect maintains global temperatures within the range needed to sustain life on earth. Without our atmosphere, the earth's average temperature would be lower by more than 30 °C (nearly 60 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate ([link](#)).



Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO<sub>2</sub> are caused by human activity, with fossil fuel burning accounting for about  $\frac{3}{4}$  of the recent increase in CO<sub>2</sub>. Reliable data from ice cores reveals that CO<sub>2</sub> concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO<sub>2</sub> concentration has increased from preindustrial levels of ~280 ppm to more than 400 ppm today ([link](#)).

### Carbon Dioxide in the Atmosphere



CO<sub>2</sub> levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

#### Note:

Click [here](#) to see a 2-minute video explaining greenhouse gases and global warming.

#### Note:

Susan Solomon

Atmospheric and climate scientist Susan Solomon ([link](#)) is the author of one of *The New York Times* books of the year (*The Coldest March*, 2001), one of Time magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica, and has authored many important papers on climate change. She has been awarded the top scientific honors in the US and France (the National Medal of Science and the Grande Medaille, respectively), and is a member of the National Academy of Sciences, the Royal Society, the French Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT, and continues to work at NOAA.

For more information, watch this [video](#) about Susan Solomon.



Susan Solomon's research focuses on climate change and has been

instrumental in determining the cause of the ozone hole over Antarctica. (credit: National Oceanic and Atmospheric Administration)

## Key Concepts and Summary

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton's law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro's law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

## Key Equations

$$P_{Total} = P_A + P_B + P_C + \dots = \sum_i P_i$$

$$P_A = X_A P_{Total}$$

$$X_A = \frac{n_A}{n_{Total}}$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

What is the density of laughing gas, dinitrogen monoxide,  $N_2O$ , at a temperature of 325 K and a pressure of 113.0 kPa?

### Exercise:

**Problem:** Calculate the density of Freon 12,  $CF_2Cl_2$ , at 30.0 °C and 0.954 atm.

#### Solution:

$$4.64 \text{ g L}^{-1}$$

### Exercise:

#### Problem:

Which is denser at the same temperature and pressure, dry air or air saturated with water vapor? Explain.

### Exercise:

**Problem:**

A cylinder of  $\text{O}_2(g)$  used in breathing by patients with emphysema has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass of oxygen is in the cylinder?

---

**Solution:**

38.8 g

**Exercise:****Problem:**

What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

**Exercise:****Problem:**

What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr?

---

**Solution:**

72.0 g mol<sup>-1</sup>

**Exercise:**

**Problem:** How could you show experimentally that the molecular formula of propene is  $\text{C}_3\text{H}_6$ , not  $\text{CH}_2$ ?

**Exercise:****Problem:**

The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP. Calculate the molar mass of this fluoride and determine its molecular formula.

---

**Solution:**

88.1 g mol<sup>-1</sup>;  $\text{PF}_3$

**Exercise:****Problem:**

Consider this question: What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies 125 mL with a pressure of 99.5 kPa at 22 °C?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

**Exercise:****Problem:**

A 36.0-L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g  $\text{CO}_2$ , 805 g  $\text{O}_2$ , and 4,880 g  $\text{N}_2$ . At 25 degrees C, what is the pressure in the cylinder in atmospheres?

---

**Solution:**

141 atm

**Exercise:**

**Problem:**

A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO<sub>2</sub>, 12.0% O<sub>2</sub>, and the remainder N<sub>2</sub> at a total pressure of 146 atm. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

**Exercise:**

**Problem:**

A sample of gas isolated from unrefined petroleum contains 90.0% CH<sub>4</sub>, 8.9% C<sub>2</sub>H<sub>6</sub>, and 1.1% C<sub>3</sub>H<sub>8</sub> at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

---

**Solution:**

CH<sub>4</sub>: 276 kPa; C<sub>2</sub>H<sub>6</sub>: 27 kPa; C<sub>3</sub>H<sub>8</sub>: 3.4 kPa

**Exercise:**

**Problem:**

A mixture of 0.200 g of H<sub>2</sub>, 1.00 g of N<sub>2</sub>, and 0.820 g of Ar is stored in a closed container at STP. Find the volume of the container, assuming that the gases exhibit ideal behavior.

**Exercise:**

**Problem:**

Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O<sub>2</sub> is not. If enough O<sub>2</sub> is added to a cylinder of H<sub>2</sub> at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?

---

**Solution:**

Yes

**Exercise:**

**Problem:**

A commercial mercury vapor analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as  $2 \times 10^{-6}$  mg/L of air. At this concentration, what is the partial pressure of gaseous mercury if the atmospheric pressure is 733 torr at 26 °C?

**Exercise:**

**Problem:**

A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18 °C. What is the pressure of the carbon monoxide? (See [link](#) for the vapor pressure of water.)

---

**Solution:**

740 torr

**Exercise:**

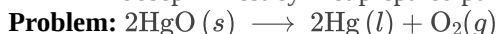


**Problem:**

In an experiment in a general chemistry laboratory, a student collected a sample of a gas over water. The volume of the gas was 265 mL at a pressure of 753 torr and a temperature of 27 °C. The mass of the gas was 0.472 g. What was the molar mass of the gas?

**Exercise:**

Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:



(a) Outline the steps necessary to answer the following question: What volume of O<sub>2</sub> at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?

(b) Answer the question.

---

**Solution:**

(a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O<sub>2</sub> produced by decomposition of this amount of HgO; and determine the volume of O<sub>2</sub> from the moles of O<sub>2</sub>, temperature, and pressure. (b) 0.308 L

**Exercise:****Problem:**

Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:

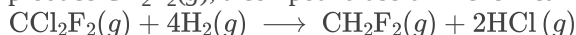
$$4\text{H}_2\text{O}(g) + 3\text{Fe}(s) \longrightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of H<sub>2</sub> at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.0 g of H<sub>2</sub>O?

(b) Answer the question.

**Exercise:****Problem:**

The chlorofluorocarbon CCl<sub>2</sub>F<sub>2</sub> can be recycled into a different compound by reaction with hydrogen to produce CH<sub>2</sub>F<sub>2</sub>(g), a compound useful in chemical manufacturing:



(a) Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton ( $1.000 \times 10^3$  kg) of CCl<sub>2</sub>F<sub>2</sub>?

(b) Answer the question.

---

**Solution:**

(a) Determine the molar mass of CCl<sub>2</sub>F<sub>2</sub>. From the balanced equation, calculate the moles of H<sub>2</sub> needed for the complete reaction. From the ideal gas law, convert moles of H<sub>2</sub> into volume. (b)  $3.72 \times 10^3$  L

**Exercise:****Problem:**

Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN<sub>3</sub>). The other product is sodium metal. Calculate the volume of nitrogen gas at 27 °C and 756 torr formed by the decomposition of 125 g of sodium azide.

**Exercise:****Problem:**

Lime, CaO, is produced by heating calcium carbonate, CaCO<sub>3</sub>; carbon dioxide is the other product.

(a) Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875° and 0.966 atm is produced by the decomposition of 1 ton ( $1.000 \times 10^3$  kg) of calcium carbonate?

(b) Answer the question.

---

**Solution:**

(a) Balance the equation. Determine the grams of CO<sub>2</sub> produced and the number of moles. From the ideal gas law, determine the volume of gas. (b)  $7.43 \times 10^5$  L

**Exercise:****Problem:**

Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C<sub>2</sub>H<sub>2</sub>, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC<sub>2</sub>, with water. The ignition of the acetylene gas provided the light. Currently, the same lamps are used by some cavers, and calcium carbide is used to produce acetylene for carbide cannons.

(a) Outline the steps necessary to answer the following question: What volume of C<sub>2</sub>H<sub>2</sub> at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC<sub>2</sub> with water?

(b) Answer the question.

**Exercise:****Problem:**

Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C<sub>2</sub>H<sub>6</sub>, to produce carbon dioxide and water, if the volumes of C<sub>2</sub>H<sub>6</sub> and O<sub>2</sub> are measured under the same conditions of temperature and pressure.

---

**Solution:**

42.00 L

**Exercise:****Problem:**

What volume of O<sub>2</sub> at STP is required to oxidize 8.0 L of NO at STP to NO<sub>2</sub>? What volume of NO<sub>2</sub> is produced at STP?

**Exercise:**

**Problem:** Consider the following questions:

(a) What is the total volume of the CO<sub>2</sub>(g) and H<sub>2</sub>O(g) at 600 °C and 0.888 atm produced by the combustion of 1.00 L of C<sub>2</sub>H<sub>6</sub>(g) measured at STP?

(b) What is the partial pressure of H<sub>2</sub>O in the product gases?

---

**Solution:**

(a) 18.0 L; (b) 0.533 atm

**Exercise:**

Methanol,  $\text{CH}_3\text{OH}$ , is produced industrially by the following reaction:



Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

**Exercise:**

**Problem:**

What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of  $\text{BaO}_2$  to  $\text{BaO}$  and  $\text{O}_2$ ?

---

**Solution:**

10.57 L  $\text{O}_2$

**Exercise:**

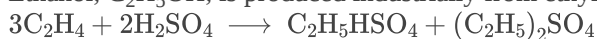
**Problem:**

A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of  $\text{N}_2$  and 1.25 L of  $\text{O}_2$  at STP. What is the colorless gas?

**Exercise:**

**Problem:**

Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is produced industrially from ethylene,  $\text{C}_2\text{H}_4$ , by the following sequence of reactions:



What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

---

**Solution:**

$5.40 \times 10^5$  L

**Exercise:**

**Problem:**

One molecule of hemoglobin will combine with four molecules of oxygen. If 1.0 g of hemoglobin combines with 1.53 mL of oxygen at body temperature ( $37^\circ\text{C}$ ) and a pressure of 743 torr, what is the molar mass of hemoglobin?

**Exercise:**

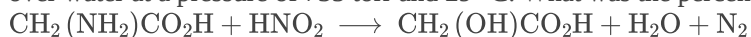
**Problem:**

A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

---

**Solution:****Exercise:****Problem:**

One method of analyzing amino acids is the van Slyke method. The characteristic amino groups ( $-\text{NH}_2$ ) in protein material are allowed to react with nitrous acid,  $\text{HNO}_2$ , to form  $\text{N}_2$  gas. From the volume of the gas, the amount of amino acid can be determined. A 0.0604-g sample of a biological sample containing glycine,  $\text{CH}_2(\text{NH}_2)\text{COOH}$ , was analyzed by the van Slyke method and yielded 3.70 mL of  $\text{N}_2$  collected over water at a pressure of 735 torr and 29 °C. What was the percentage of glycine in the sample?

**Glossary**

Dalton's law of partial pressures

total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

mole fraction ( $X$ )

concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

partial pressure

pressure exerted by an individual gas in a mixture

vapor pressure of water

pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

## Kinetic-Molecular Theory

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term “molecule” will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the

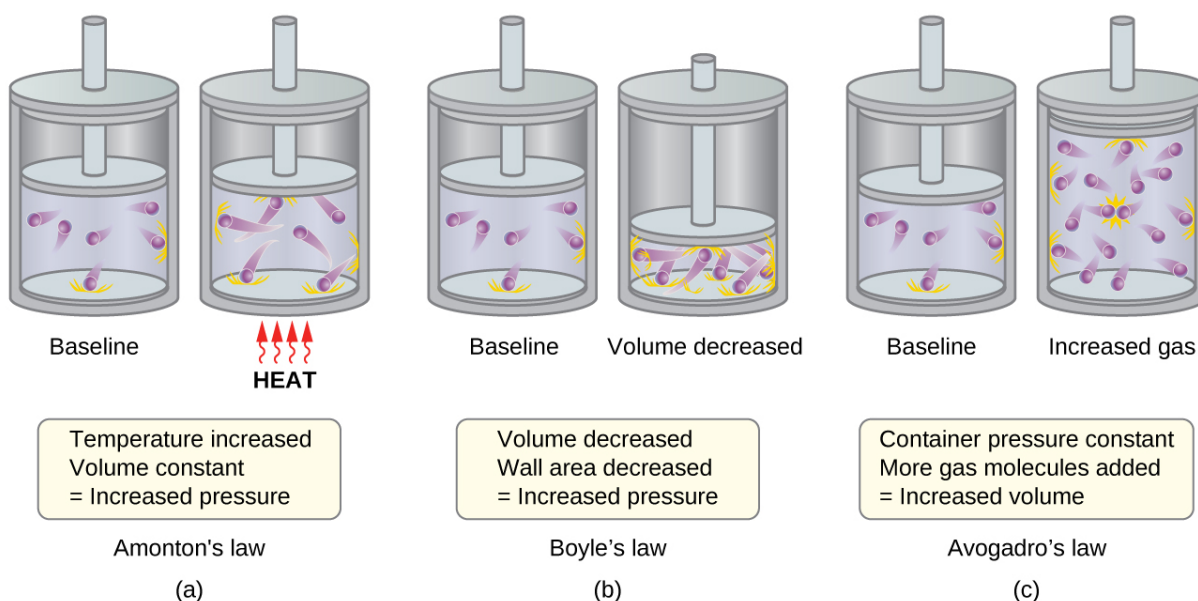
KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

## The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure ([\[link\]](#)).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas ([\[link\]](#)).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions ([\[link\]](#)).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the

total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.



(a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

## Key Concepts and Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the

distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

### Exercise:

#### Problem:

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

---

#### Solution:

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

### Exercise:

#### Problem:

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

- (a) The pressure of the gas is increased by reducing the volume at constant temperature.
- (b) The pressure of the gas is increased by increasing the temperature at constant volume.
- (c) The average velocity of the molecules is increased by a factor of 2.



## Glossary

kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

root mean square velocity ( $u_{\text{rms}}$ )

measure of average velocity for a group of particles calculated as the square root of the average squared velocity

## Non-Ideal Gas Behavior - Optional Reading

By the end of this section, you will be able to:

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility ( $Z$ ) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

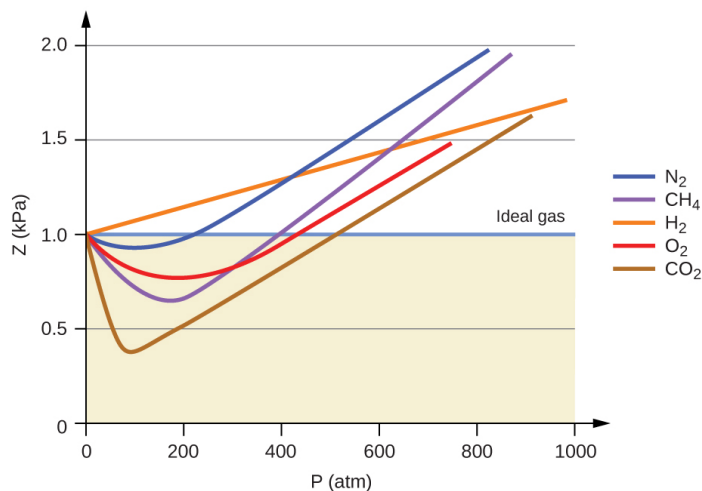
Thus far, the ideal gas law,  $PV = nRT$ , has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of  $PV = nRT$  can be judged is by comparing the actual volume of 1 mole of gas (its molar volume,  $V_m$ ) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor ( $Z$ )** with:

**Equation:**

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left( \frac{PV_m}{RT} \right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. [\[link\]](#) shows plots of  $Z$  over a large pressure range for several common gases.

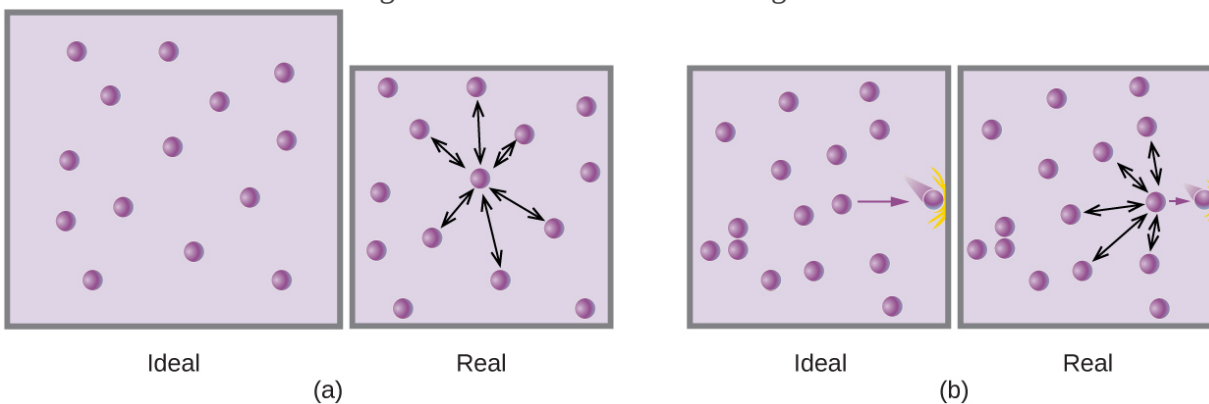


A graph of the compressibility factor ( $Z$ ) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from [\[link\]](#), the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas. The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) ([\[link\]](#)). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.



(a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted at constant volume compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Correction for molecular attraction
Correction for volume of molecules

The constant  $a$  corresponds to the strength of the attraction between molecules of a particular gas, and the constant  $b$  corresponds to the size of the molecules of a particular gas. The “correction” to the pressure term in the ideal gas law is  $\frac{n^2a}{V^2}$ , and the “correction” to the volume is  $nb$ . Note that when  $V$  is relatively large and  $n$  is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law,  $PV = nRT$ . Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in [\[link\]](#).

Values of van der Waals Constants for Some Common Gases		
Gas	$a$ (L <sup>2</sup> atm/mol <sup>2</sup> )	$b$ (L/mol)
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
CO <sub>2</sub>	3.59	0.0427
H <sub>2</sub> O	5.46	0.0305
He	0.0342	0.0237
CCl <sub>4</sub>	20.4	0.1383

At low pressures, the correction for intermolecular attraction,  $a$ , is more important than the one for molecular volume,  $b$ . At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by  $PV = nRT$  over a small range of pressures. This behavior is reflected by the “dips” in several of the compressibility curves shown in [\[link\]](#). The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised ( $Z$  decreases with increasing  $P$ ). At very high pressures, the gas becomes less compressible ( $Z$  increases with  $P$ ), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

**Example:**

**Comparison of Ideal Gas Law and van der Waals Equation**

A 4.25-L flask contains 3.46 mol CO<sub>2</sub> at 229 °C. Calculate the pressure of this sample of CO<sub>2</sub>:

- (a) from the ideal gas law
- (b) from the van der Waals equation
- (c) Explain the reason(s) for the difference.

**Solution**

(a) From the ideal gas law:

**Equation:**

$$P = \frac{nRT}{V} = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{4.25 \text{ L}} = 33.5 \text{ atm}$$

(b) From the van der Waals equation:

**Equation:**

$$\left( P + \frac{n^2 a}{V^2} \right) \times (V - nb) = nRT \longrightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

**Equation:**

$$P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^{-2}}{(4.25 \text{ L})^2}$$

This finally yields  $P = 32.4 \text{ atm}$ .

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO<sub>2</sub> molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

**Check your Learning**

A 560-mL flask contains 21.3 g N<sub>2</sub> at 145 °C. Calculate the pressure of N<sub>2</sub>:

- (a) from the ideal gas law
- (b) from the van der Waals equation
- (c) Explain the reason(s) for the difference.

**Note:**

**Answer:**

(a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

## Key Concepts and Summary

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under these conditions.

## Key Equations

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left( \frac{P \times V_m}{R \times T} \right)_{\text{measured}}$$

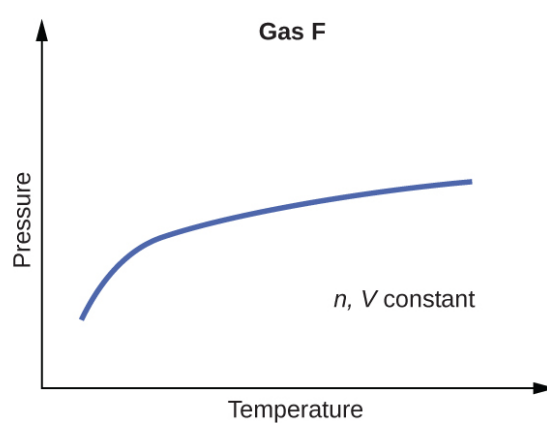
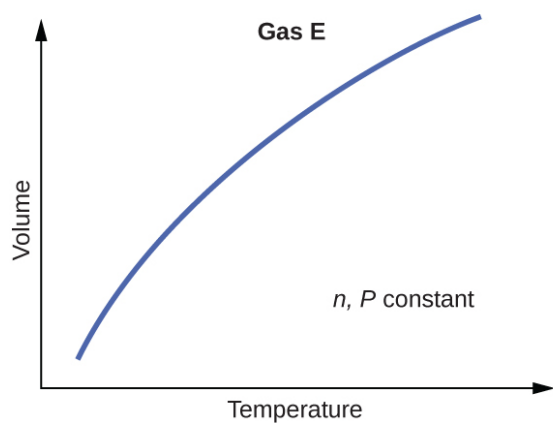
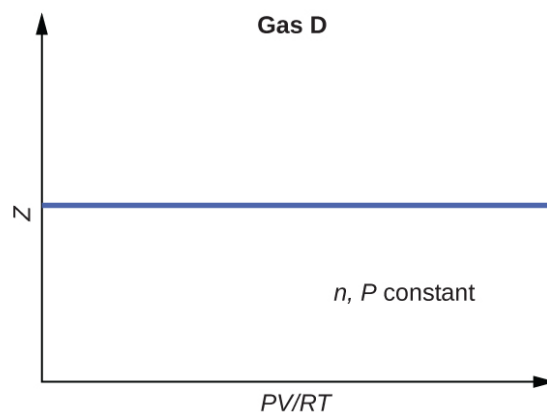
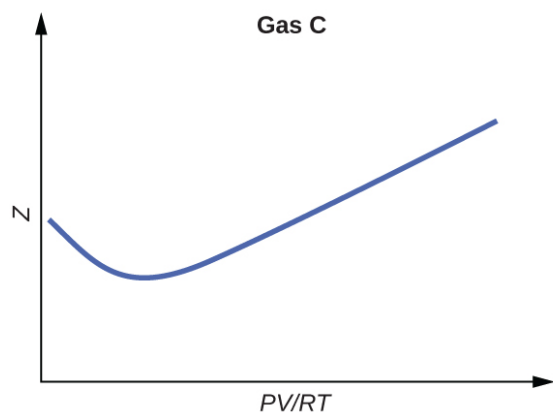
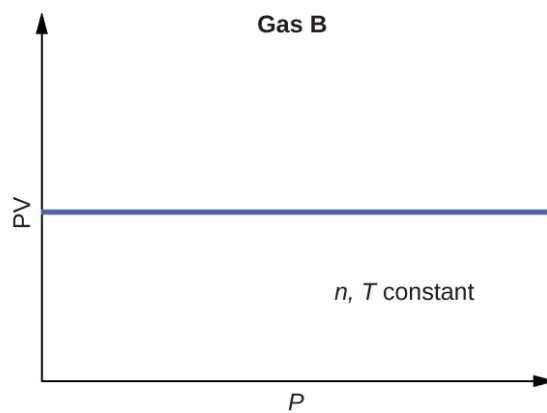
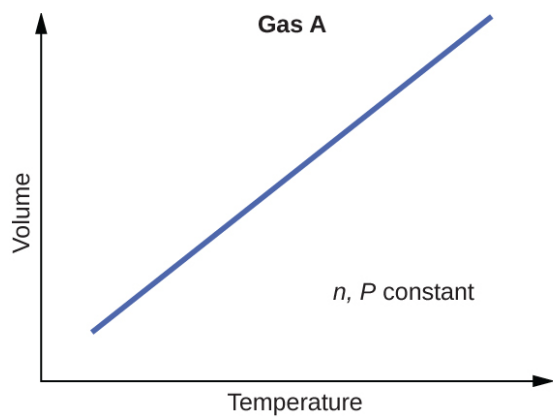
$$\left( P + \frac{n^2 a}{V^2} \right) \times (V - nb) = nRT$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?



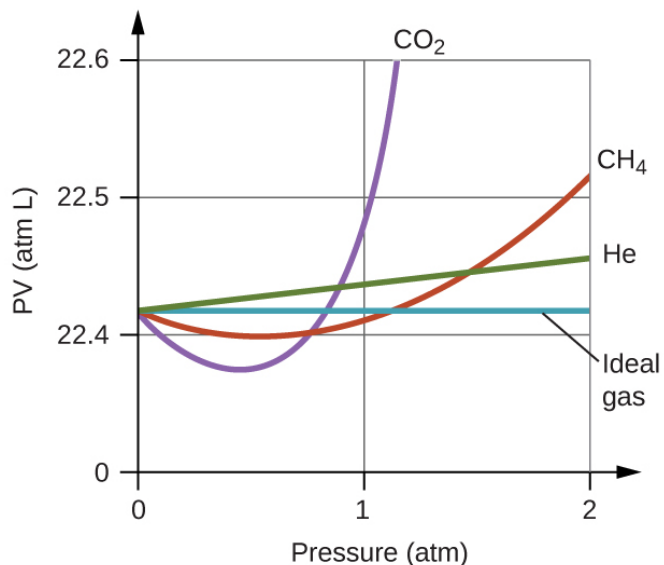

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**Solution:**

Gases C, E, and F

**Exercise:**

**Problem:** Explain why the plot of  $PV$  for  $\text{CO}_2$  differs from that of an ideal gas.



**Exercise:**

**Problem:**

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

- (a) high pressure, small volume
- (b) high temperature, low pressure
- (c) low temperature, high pressure

---

**Solution:**

The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

**Exercise:**

**Problem:**

Describe the factors responsible for the deviation of the behavior of real gases from that of an ideal gas.

**Exercise:**

**Problem:**

For which of the following gases should the correction for the molecular volume be largest:



CO, CO<sub>2</sub>, H<sub>2</sub>, He, NH<sub>3</sub>, SF<sub>6</sub>?

---

**Solution:**

SF<sub>6</sub>

**Exercise:**

**Problem:** A 0.245-L flask contains 0.467 mol CO<sub>2</sub> at 159 °C. Calculate the pressure:

- (a) using the ideal gas law
- (b) using the van der Waals equation
- (c) Explain the reason for the difference.
- (d) Identify which correction (that for P or V) is dominant and why.

**Exercise:**

**Problem:** Answer the following questions:

- (a) If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
- (b) For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
- (c) What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
- (d) What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
- (e) In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

---

**Solution:**

(a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures, they behave close enough to ideal gases that they are approximated as such; however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation. (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see [\[link\]](#)). (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and

low temperatures, the effect of intermolecular attractions would be larger. See [\[link\]](#). (e) Low temperatures

## Glossary

compressibility factor ( $Z$ )

ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

van der Waals equation

modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

## Introduction

class="introduction"

- Energy Basics
- Calorimetry
- Enthalpy

Sliding a  
match head  
along a  
rough  
surface  
initiates a  
combustion  
reaction that  
produces  
energy in  
the form of  
heat and  
light.  
(credit:  
modificatio  
n of work  
by Laszlo  
Ilyes)



Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[\[footnote\]](#) While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.

US Energy Information Administration, *Primary Energy Consumption by Source and Sector*, 2012,

[http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css\\_2012\\_energy.pdf](http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css_2012_energy.pdf)  
. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

The chemical bond is simply another form of energy, and its strength is indicated in exactly the same units as any other process involving energy. That is, in joules (or kilojoules) – or, when taken on a molar basis, in J/mol or kJ/mol. All of the principles involving energy we have examined up to now apply to bond energies exactly as they do to all other forms of energy: that is, energy may change form or be absorbed or released, but it cannot be created or destroyed. The energy of a chemical bond is indicated by the bond enthalpy, taken by convention to be the energy required to break a chemical bond. The same energy is released when a chemical bond is formed. Given that a chemical reaction involves breaking some bonds and making others, the enthalpy change for a chemical reaction can be estimated by analyzing the bonds broken and formed during the reaction. While this procedure gives an estimate of the overall enthalpy, it should be noted that a far more precise method involves using enthalpies of formation; the fact that there can be significant differences between, for example, an O–H bond in water and that in acetic acid accounts for the discrepancy in calculating  $\Delta H$  using bond enthalpies versus the use of enthalpies of formation.

## Energy Basics

By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

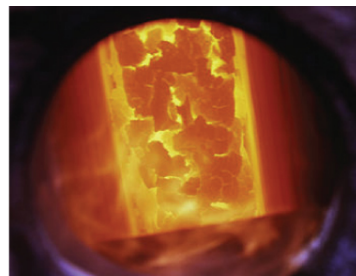
Chemical changes and their accompanying changes in energy are important parts of our everyday world ([\[link\]](#)). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a)



(b)



(c)

The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by

“Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

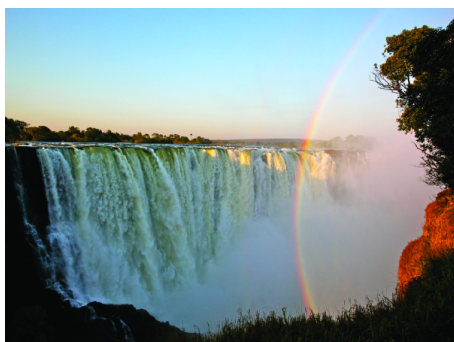
This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

## Energy

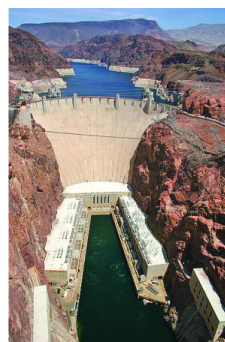
**Energy** can be defined as the capacity to supply heat or do work. One type of **work (w)** is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move

matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant ([link](#)). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a)



(b)

(a) Water at a higher elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons)



Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

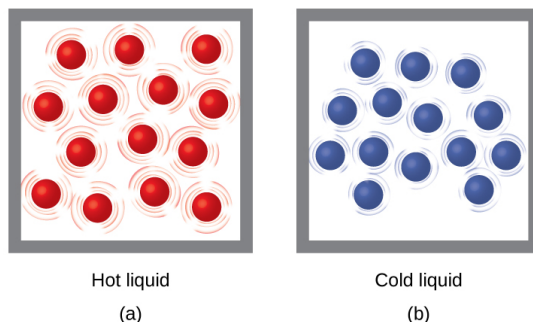
When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry.

## **Thermal Energy, Temperature, and Heat**

**Thermal energy** is kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is “cold” ([\[link\]](#)). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no

chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.



(a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

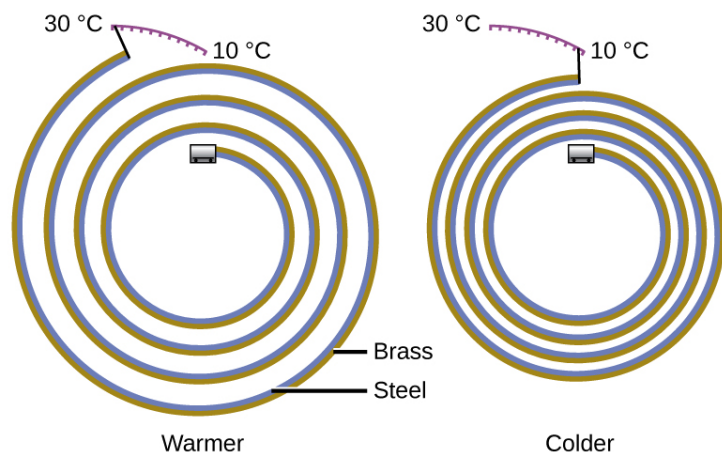
**Note:**

Click on this [interactive simulation](#) to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in [\[link\]](#). The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.



(a)



(b)

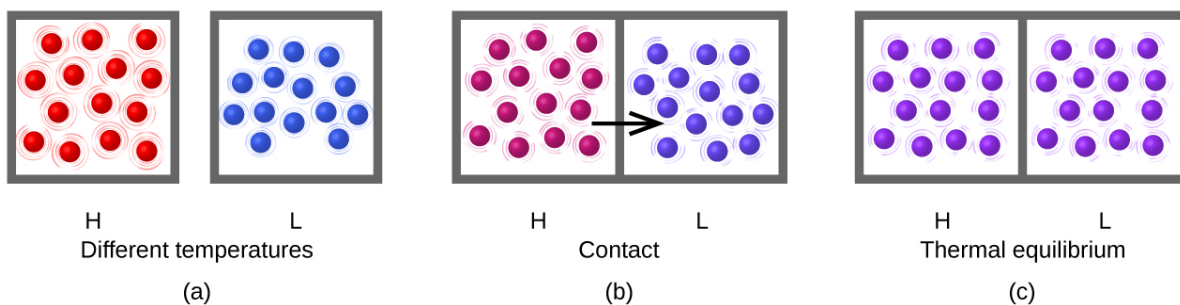
(a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

**Note:**

The following [demonstration](#) allows one to view the effects of heating and cooling a coiled bimetallic strip.

**Heat ( $q$ )** is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy)

substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature ([\[link\]](#)).



(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature and their molecules have the same average kinetic energy.

**Note:**

Click on the [PhET simulation](#) to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame ([link](#)). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



(a)



(b)

(a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by “Skatebiker”/Wikimedia commons)

Historically, energy was measured in units of **calories (cal)**. A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and

the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to  $1 \text{ kg m}^2/\text{s}^2$ , which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity (C)** of a body of matter is the quantity of heat ( $q$ ) it absorbs or releases when it experiences a temperature change ( $\Delta T$ ) of 1 degree Celsius (or equivalently, 1 kelvin):

**Equation:**

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

**Equation:**

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 363 \text{ J}/^{\circ}\text{C}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

**Equation:**

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 1814 \text{ J/}^{\circ}\text{C}$$

The **specific heat capacity (c)** of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

**Equation:**

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

**Equation:**

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

**Equation:**

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4040 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$



Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of  $\text{J/mol } ^\circ\text{C}$  ([\[link\]](#)).



Because of its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

water has a relatively high specific heat (about  $4.2 \text{ J/g } ^\circ\text{C}$  for the liquid and  $2.09 \text{ J/g } ^\circ\text{C}$  for the solid)); most metals have much lower specific heats (usually less than  $1 \text{ J/g } ^\circ\text{C}$ ). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in [\[link\]](#).

---



Specific Heats of Common Substances at 25 °C and 1 bar		
Substance	Symbol ( <i>state</i> )	Specific Heat (J/g °C)
helium	He( <i>g</i> )	5.193
water	H <sub>2</sub> O( <i>l</i> )	4.184
ethanol	C <sub>2</sub> H <sub>6</sub> O( <i>l</i> )	2.376
ice	H <sub>2</sub> O( <i>s</i> )	2.093 (at −10 °C)
water vapor	H <sub>2</sub> O( <i>g</i> )	1.864
nitrogen	N <sub>2</sub> ( <i>g</i> )	1.040
air		1.007
oxygen	O <sub>2</sub> ( <i>g</i> )	0.918
aluminum	Al( <i>s</i> )	0.897
carbon dioxide	CO <sub>2</sub> ( <i>g</i> )	0.853
argon	Ar( <i>g</i> )	0.522
iron	Fe( <i>s</i> )	0.449
copper	Cu( <i>s</i> )	0.385
lead	Pb( <i>s</i> )	0.130
gold	Au( <i>s</i> )	0.129
silicon	Si( <i>s</i> )	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat,  $q$ , entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

**Equation:**

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation,  $c$  is the specific heat of the substance,  $m$  is its mass, and  $\Delta T$  (which is read “delta T”) is the temperature change,  $T_{\text{final}} - T_{\text{initial}}$ . If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature,  $T_{\text{final}} - T_{\text{initial}}$  has a positive value, and the value of  $q$  is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature,  $T_{\text{final}} - T_{\text{initial}}$  has a negative value, and the value of  $q$  is negative.

**Example:**

**Measuring Heat**

A flask containing  $8.0 \times 10^2$  g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

**Solution**

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case,  $8.0 \times 10^2$  g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat  $8.0 \times 10^2$  g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water

by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

**Equation:**

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

**Equation:**

$$\begin{aligned} &= (4.184 \text{ J/g} \cdot ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (85 - 21) ^\circ\text{C} \\ &= (4.184 \text{ J/g} \cdot ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (64) ^\circ\text{C} \\ &= 210,000 \text{ J} (= 2.1 \times 10^5 \text{ kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and  $q$  is positive.

### Check Your Learning

How much heat, in joules, must be added to a 502 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

**Note:**

**Answer:**

$$5.12 \times 10^6 \text{ J}$$

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

**Example:****Determining Other Quantities**

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C.

Determine the specific heat of this metal (which might provide a clue to its identity).

**Solution**

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

**Equation:**

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

**Equation:**

$$6640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) ^\circ\text{C}$$

Solving:

**Equation:**

$$c = \frac{6640 \text{ J}}{(348 \text{ g}) \times (21.2 ^\circ\text{C})} = 0.900 \text{ J/g } ^\circ\text{C}$$

Comparing this value with the values in [\[link\]](#), this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

**Check Your Learning**

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C.

Determine the specific heat of this metal, and predict its identity.

**Note:****Answer:**

$c = 0.451 \text{ J/g } ^\circ\text{C}$ ; the metal is likely to be iron

**Note:**

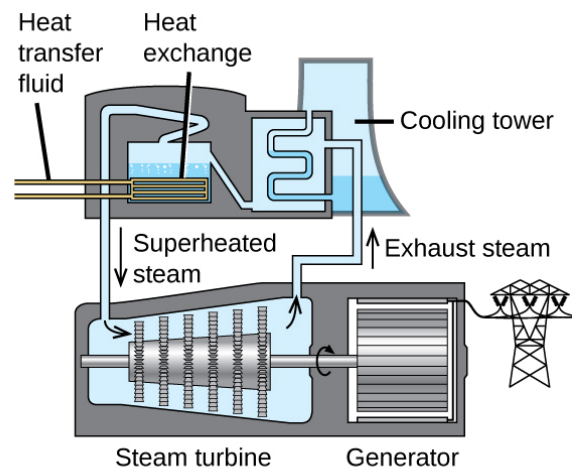
### Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat “stored” in that substance is then converted into electricity.

The Solana Generating Station in Arizona’s Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) ([link](#)). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.



(a)



(b)

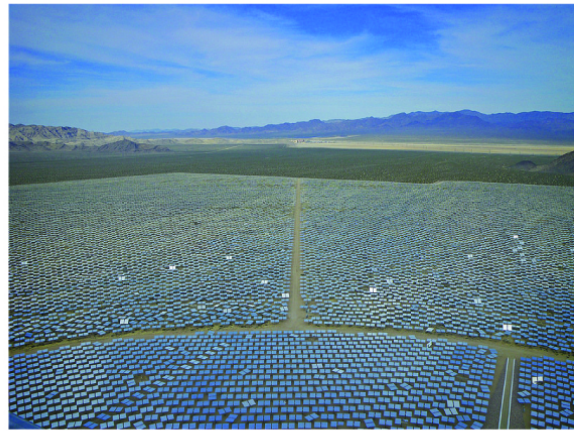
This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land

## Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world ([\[link\]](#)). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a)



(b)

(a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border.

(credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

## Key Concepts and Summary

Energy is the capacity to supply heat or do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is

converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

The thermal energy of matter is due to the kinetic energies of its constituent atoms or molecules. Temperature is an intensive property of matter reflecting hotness or coldness that increases as the average kinetic energy increases. Heat is the transfer of thermal energy between objects at different temperatures. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

## Key Equations

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

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#### Solution:

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

**Exercise:**

**Problem:**

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

**Exercise:**

**Problem:**

Explain the difference between heat capacity and specific heat of a substance.

---

**Solution:**

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

**Exercise:**

**Problem:**

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 28.4 g of water

(b) 1.00 oz of lead



**Exercise:****Problem:**

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

---

**Solution:**

(a) 47.6 J/°C; 11.38 cal °C<sup>-1</sup>; (b) 407 J/°C; 97.3 cal °C<sup>-1</sup>

**Exercise:****Problem:**

How much heat, in joules and in calories, must be added to a 75.0-g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

**Exercise:****Problem:**

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from -23.0 °C to -1.0 °C?

---

**Solution:**

1310 J; 313 cal

**Exercise:****Problem:**

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

**Exercise:**

**Problem:**

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

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**Solution:**

7.15 °C

**Exercise:****Problem:**

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

- (a) What is the specific heat of the substance?
- (b) If it is one of the substances found in [\[link\]](#), what is its likely identity?

**Exercise:****Problem:**

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

- (a) What is the specific heat of the substance?
  - (b) If it is one of the substances found in [\[link\]](#), what is its likely identity?
- 

**Solution:**

- (a) 0.390 J/g °C; (b) Copper is a likely candidate.

**Exercise:**

**Problem:** An aluminum kettle weighs 1.05 kg.

- (a) What is the heat capacity of the kettle?
- (b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
- (c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

**Exercise:**

**Problem:**

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) =  $3.6 \times 10^6$  J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

---

**Solution:**

We assume that the density of water is 1.0 g/cm<sup>3</sup>(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated.  
Energy required = 7.47 kWh

**Glossary**

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat ( $q$ )

transfer of thermal energy between two bodies

heat capacity ( $C$ )

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second,  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$  and  $4.184 \text{ J} = 1 \text{ cal}$

kinetic energy

energy of a moving body, in joules, equal to  $\frac{1}{2}mv^2$  (where  $m$  = mass and  $v$  = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity ( $c$ )

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work ( $w$ )

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

## Enthalpy or Heat

By the end of this section, you will be able to:

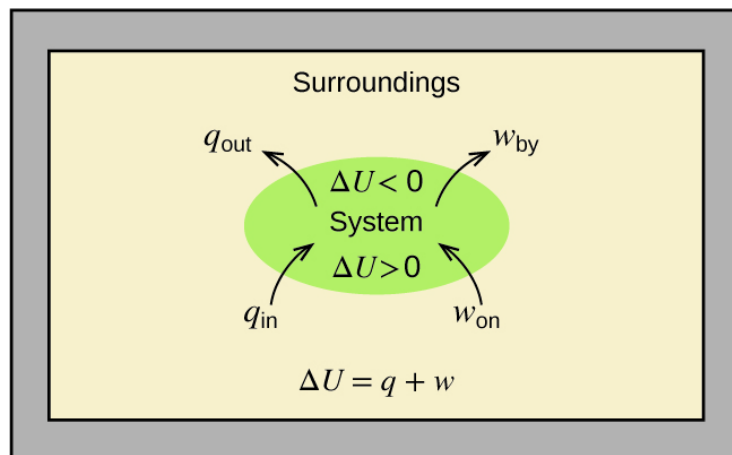
- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of **chemical thermodynamics**, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the **internal energy ( $U$ )**, sometimes symbolized as  $E$ .

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat ( $q$ ) from the surroundings or when the surroundings do work ( $w$ ) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

as shown in [\[link\]](#). This is one version of the **first law of thermodynamics**, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive  $q$  is heat flow in; negative  $q$  is heat flow out) or work done on or by the system. The work,  $w$ , is positive if it is done on the system and negative if it is done by the system.



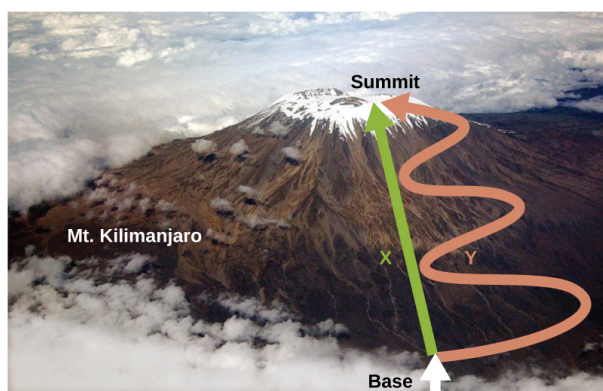
The internal energy,  $U$ , of a system can be changed by heat flow and work. If heat flows into the system,  $q_{\text{in}}$ , or work is done on the system,  $w_{\text{on}}$ , its internal energy increases,  $\Delta U > 0$ . If heat flows out of the system,  $q_{\text{out}}$ , or work is done by the system,  $w_{\text{by}}$ , its internal energy decreases,  $\Delta U < 0$ .

A type of work called **expansion work** (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

**Note:**

This view of [an internal combustion engine](#) illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as  $\Delta U = q + w$ . Internal energy is an example of a **state function** (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path ([link](#)). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).



Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as **enthalpy ( $H$ )** to describe the thermodynamics of chemical and physical processes.

Enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. We will focus on simplified changes in enthalpy.

For the heat processes focused on in this course, the heat flow ( $q_p$ ) and enthalpy change ( $\Delta H$ ) for the process are equal.

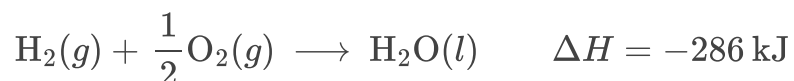


The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter ([\[link\]](#)) is not equal to  $\Delta H$  because the closed, constant-volume metal container prevents the pressure from remaining constant (it may increase or decrease if the reaction yields increased or decreased amounts of gaseous species). Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with  $q = \Delta H$ , which makes enthalpy the most convenient choice for determining heat changes for chemical reactions.

The following conventions apply when using  $\Delta H$ :

- A negative value of an enthalpy change,  $\Delta H < 0$ , indicates an exothermic reaction; a positive value,  $\Delta H > 0$ , indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its  $\Delta H$  is changed (a process that is endothermic in one direction is exothermic in the opposite direction).
- Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a  $\Delta H$  value following the equation for the reaction. This  $\Delta H$  value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

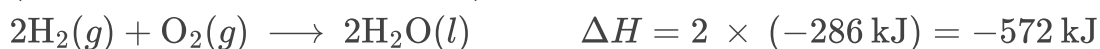
**Equation:**



This equation indicates that when 1 mole of hydrogen gas and  $\frac{1}{2}$  mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor ( $\Delta H$  is an extensive property):

**Equation:**

(two-fold increase in amounts)

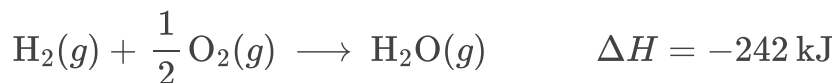


(two-fold decrease in amounts)



- The enthalpy change of a reaction depends on the physical states of the reactants and products, so these must be shown. For example, when 1 mole of hydrogen gas and  $\frac{1}{2}$  mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

**Equation:**

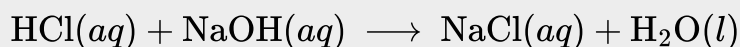


**Example:**

### Writing Thermochemical Equations

When 0.0500 mol of  $\text{HCl}(aq)$  reacts with 0.0500 mol of  $\text{NaOH}(aq)$  to form 0.0500 mol of  $\text{NaCl}(aq)$ , 2.9 kJ of heat are produced. Write a balanced thermochemical equation for the reaction of one mole of  $\text{HCl}$ .

**Equation:**



### Solution

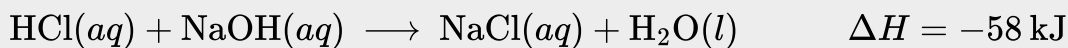
For the reaction of 0.0500 mol acid ( $\text{HCl}$ ),  $q = -2.9 \text{ kJ}$ . The reactants are provided in stoichiometric amounts (same molar ratio as in the balanced equation), and so the amount of acid may be used to calculate a molar enthalpy change. Since  $\Delta H$  is an extensive property, it is proportional to the amount of acid neutralized:

**Equation:**

$$\Delta H = 1 \text{ mol HCl} \times \frac{-2.9 \text{ kJ}}{0.0500 \text{ mol HCl}} = -58 \text{ kJ}$$

The thermochemical equation is then

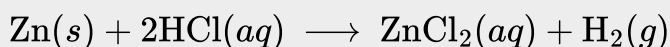
**Equation:**



### Check Your Learning

When 1.34 g  $\text{Zn}(s)$  reacts with 60.0 mL of 0.750 M  $\text{HCl}(aq)$ , 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

**Equation:**



**Note:**

**Answer:**

$$\Delta H = -153 \text{ kJ}$$

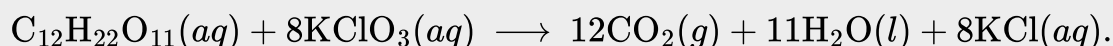
Be sure to take both stoichiometry and limiting reactants into account when determining the  $\Delta H$  for a chemical reaction.

**Example:**

**Writing Thermochemical Equations**

A gummy bear contains 2.67 g sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . When it reacts with 7.19 g potassium chlorate,  $\text{KClO}_3$ , 43.7 kJ of heat are produced. Write a thermochemical equation for the reaction of one mole of sucrose:

**Equation:**



**Solution**

Unlike the previous example exercise, this one does not involve the reaction of stoichiometric amounts of reactants, and so the *limiting reactant* must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are

**Equation:**

$$(2.67 \text{ g}) (1 \text{ mol}/342.3 \text{ g}) = 0.00780 \text{ mol } \text{C}_{12} \text{H}_{22} \text{O}_{11}$$

$$(7.19 \text{ g}) (1 \text{ mol}/122.5 \text{ g}) = 0.0587 \text{ mol } \text{KClO}_3$$

The provided molar ratio of perchlorate-to-sucrose is then

**Equation:**

$$0.0587 \text{ mol } \text{KClO}_3 / 0.00780 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11} = 7.52$$

The balanced equation indicates 8 mol  $\text{KClO}_3$  are required for reaction with 1 mol  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . Since the provided amount of  $\text{KClO}_3$  is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

**Equation:**

$$\Delta H = -43.7 \text{ kJ}/0.0587 \text{ mol KClO}_3 = 744 \text{ kJ/mol KClO}_3$$

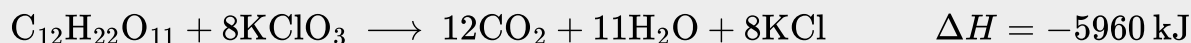
Because the equation, as written, represents the reaction of 8 mol KClO<sub>3</sub>, the enthalpy change is

**Equation:**

$$(744 \text{ kJ/mol KClO}_3) (8 \text{ mol KClO}_3) = 5960 \text{ kJ}$$

The enthalpy change for this reaction is -5960 kJ, and the thermochemical equation is:

**Equation:**



### Check Your Learning

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of FeCl<sub>2</sub>(s) and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of FeCl<sub>2</sub>(s) is produced?

**Note:**

**Answer:**

$$\Delta H = -338 \text{ kJ}$$

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the  $\Delta H$  of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm),  $\Delta H$  values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted “o” in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, this temperature will be assumed unless some other temperature is specified. Thus, the symbol ( $\Delta H^\circ$ ) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol  $\Delta H$  is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the  $\Delta H$  for specific amounts of reactants). However, we often find it more useful to divide one extensive property ( $\Delta H$ ) by another (amount of substance), and report a per-amount *intensive* value of  $\Delta H$ , often “normalized” to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

## Key Concepts and Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction,  $q$  for the change is called the enthalpy change with the symbol  $\Delta H$ , or  $\Delta H^\circ$  for reactions occurring under standard state conditions at 298 K. The value of  $\Delta H$  for a reaction in one direction is equal in magnitude, but opposite in sign, to  $\Delta H$  for the reaction in the opposite direction, and  $\Delta H$  is directly proportional to the quantity of reactants and products.

## Glossary

chemical thermodynamics

area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy ( $H$ )

sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change ( $\Delta H$ )

heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)

work done as a system expands or contracts against external pressure

first law of thermodynamics

internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law

if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon

compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy ( $U$ )

total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion ( $\Delta H_c^\circ$ )

heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation ( $\Delta H_f^\circ$ )

enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state

set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function

property depending only on the state of a system, and not the path taken to reach that state

## Introduction

class="introduction"

- Intermolecular Forces
- Properties of Liquids
- Phase Transitions
- Phase Diagrams
- The Solid State of Matter
- Lattice Structures in Crystalline Solids

Solid carbon  
dioxide

("dry ice",  
left)

sublimes  
vigorously  
when placed  
in a liquid  
(right),  
cooling the  
liquid and  
generating a  
dense mist  
of water  
above the  
cylinder.

(credit:  
modificatio  
n of work  
by Paul  
Flowers)



The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.



## Intermolecular Forces

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

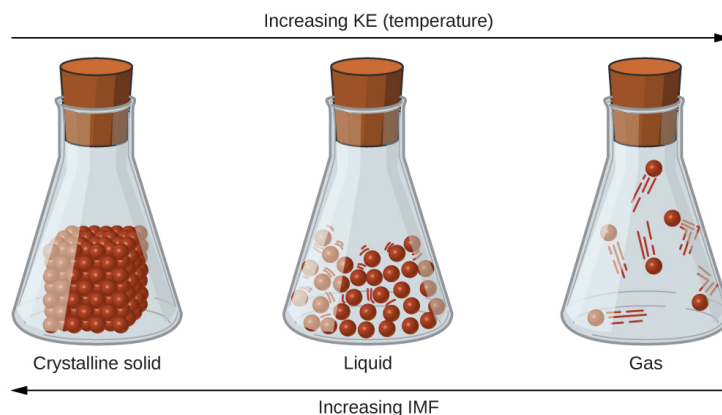
As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase “intermolecular attraction” to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy

required to overcome the attractive forces and thus increase the distance between particles. [\[link\]](#) illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

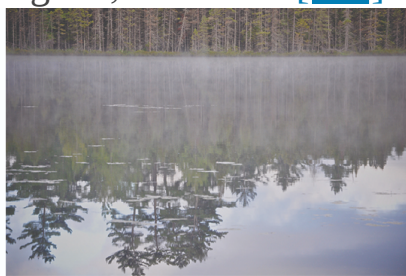


Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between  $\text{H}_2\text{O}$  molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid  $\text{H}_2\text{O}$ . For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in [\[link\]](#).



(a)



(b)

Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane,  $C_4H_{10}$ , is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in [\[link\]](#).



Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by “Sam-Cat”/Flickr)

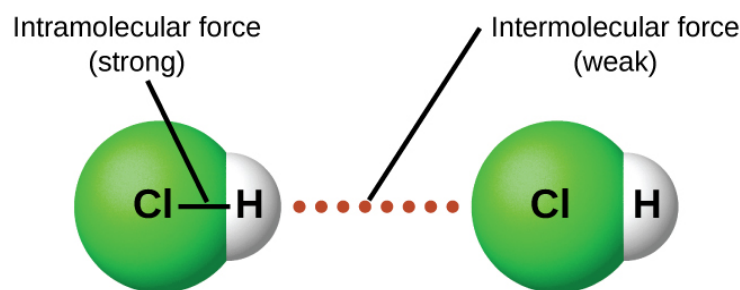
Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

**Note:**

Access this [interactive simulation](#) on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

## Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intramolecular* forces. *Intramolecular* forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Intermolecular* forces are the attractions *between* molecules, which determine many of the physical properties of a substance. [\[link\]](#) illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

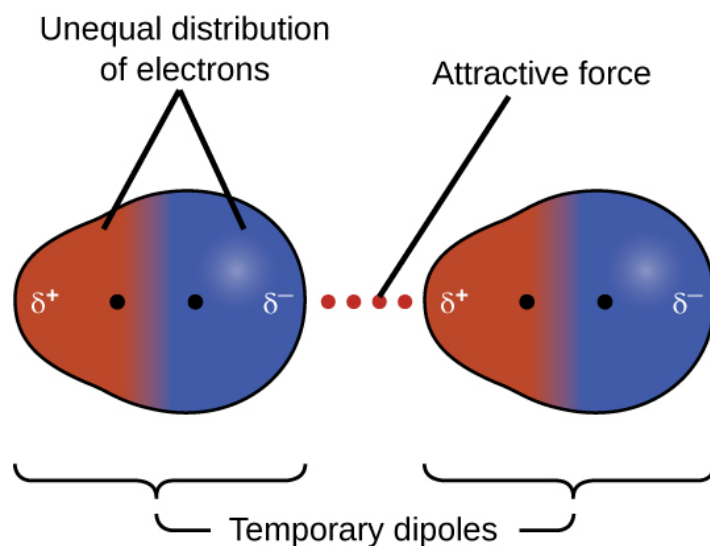


*Intramolecular* forces keep a molecule intact. *Intermolecular* forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

## Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in [\[link\]](#).



Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules.  $\text{F}_2$  and  $\text{Cl}_2$  are gases at room temperature (reflecting weaker attractive forces);  $\text{Br}_2$  is a liquid, and  $\text{I}_2$  is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in [\[link\]](#).

### Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F <sub>2</sub>	38 g/mol	72 pm	53 K	85 K
chlorine, Cl <sub>2</sub>	71 g/mol	99 pm	172 K	238 K
bromine, Br <sub>2</sub>	160 g/mol	114 pm	266 K	332 K
iodine, I <sub>2</sub>	254 g/mol	133 pm	387 K	457 K
astatine, At <sub>2</sub>	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.



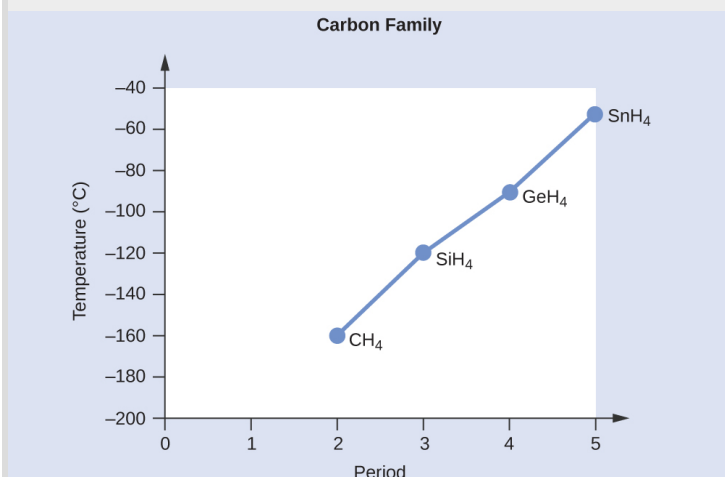
**Example:****London Forces and Their Effects**

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point:  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$ , and  $\text{SnH}_4$ . Explain your reasoning.

**Solution**

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$ , and  $\text{SnH}_4$  are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore,  $\text{CH}_4$  is expected to have the lowest boiling point and  $\text{SnH}_4$  the highest boiling point. The ordering from lowest to highest boiling point is expected to be  $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$ .

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:

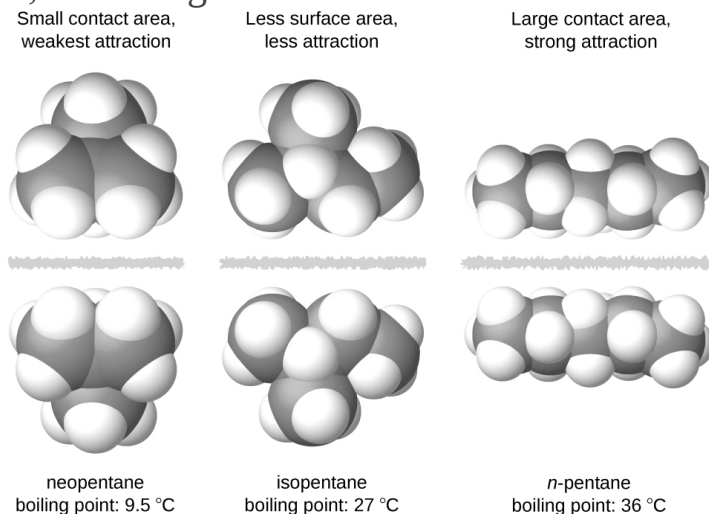
**Check Your Learning**

Order the following hydrocarbons from lowest to highest boiling point:  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{C}_4\text{H}_{10}$ .

**Note:****Answer:**

$C_2H_6 < C_3H_8 < C_4H_{10}$ . All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore  $C_2H_6 < C_3H_8 < C_4H_{10}$ .

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in [\[link\]](#)) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula,  $C_5H_{12}$ , the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.



The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

**Note:**

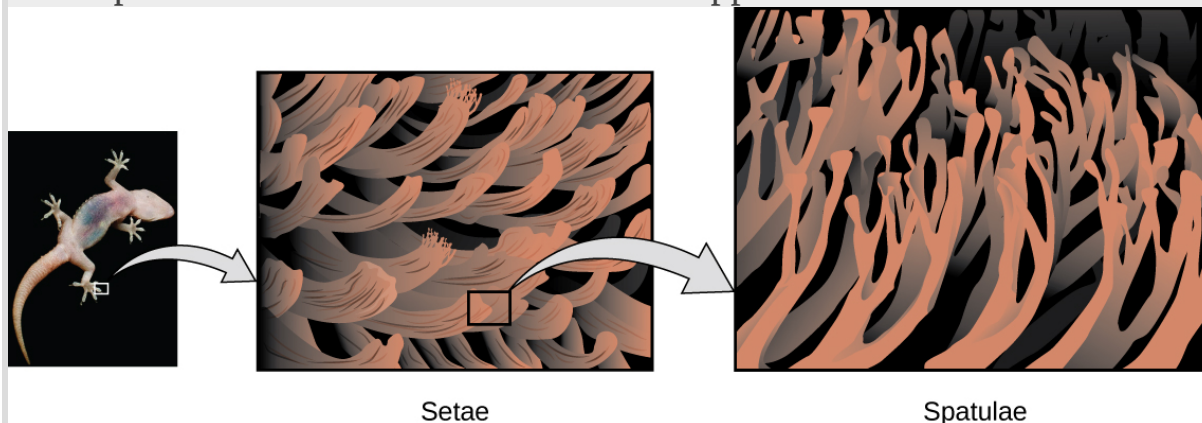
**Geckos and Intermolecular Forces**

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in [\[link\]](#), with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from “sticky” to “non-sticky.” Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small

shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC\*+A!"/Flickr)

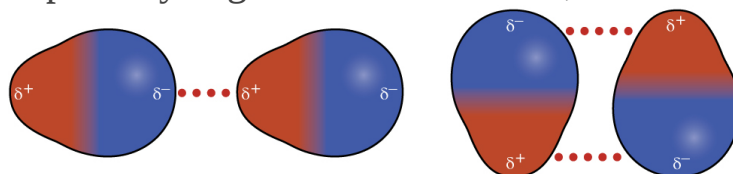
### **Note:**

Watch this [video](#) to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

## **Dipole-Dipole Attractions**

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge

called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in [\[link\]](#).



This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F<sub>2</sub> molecules. Both HCl and F<sub>2</sub> consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F<sub>2</sub> molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F<sub>2</sub> (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F<sub>2</sub> molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

**Example:****Dipole-Dipole Forces and Their Effects**

Predict which will have the higher boiling point:  $\text{N}_2$  or  $\text{CO}$ . Explain your reasoning.

**Solution**

$\text{CO}$  and  $\text{N}_2$  are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because  $\text{CO}$  is a polar molecule, it experiences dipole-dipole attractions. Because  $\text{N}_2$  is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between  $\text{CO}$  molecules are comparably stronger than the dispersion forces between nonpolar  $\text{N}_2$  molecules, so  $\text{CO}$  is expected to have the higher boiling point.

**Check Your Learning**

Predict which will have the higher boiling point:  $\text{ICl}$  or  $\text{Br}_2$ . Explain your reasoning.

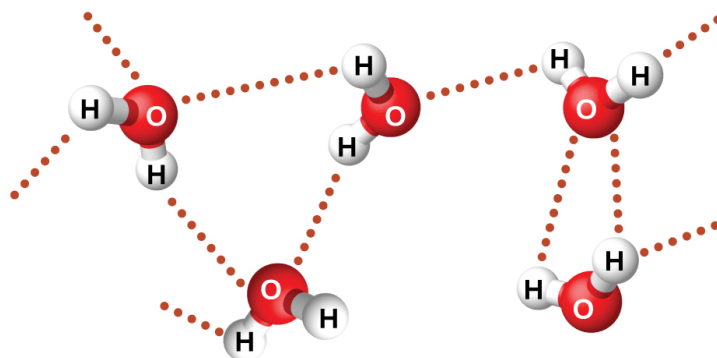
**Note:****Answer:**

$\text{ICl}$ .  $\text{ICl}$  and  $\text{Br}_2$  have similar masses ( $\sim 160$  amu) and therefore experience similar London dispersion forces.  $\text{ICl}$  is polar and thus also exhibits dipole-dipole attractions;  $\text{Br}_2$  is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so  $\text{ICl}$  will have the higher boiling point.

## Hydrogen Bonding

Nitrosyl fluoride ( $\text{ONF}$ , molecular mass 49 amu) is a gas at room temperature. Water ( $\text{H}_2\text{O}$ , molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and  $\text{ONF}$  is the heavier and larger molecule. It is,

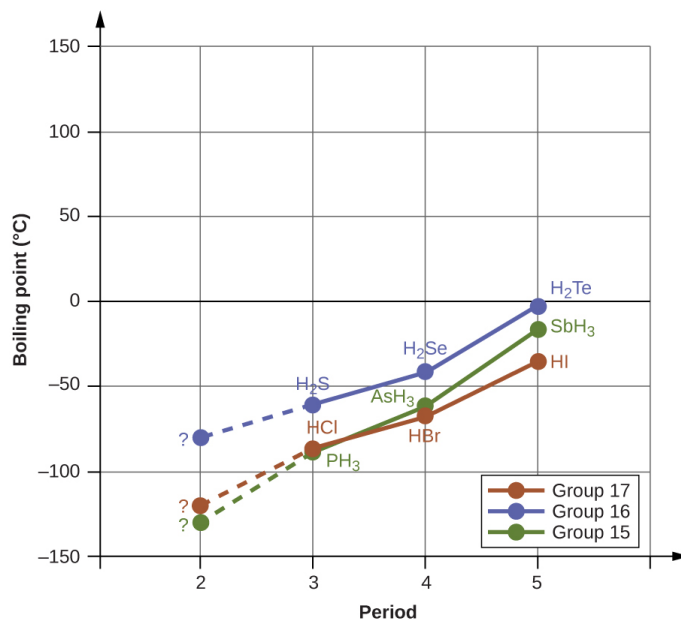
therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include  $\text{HF}\cdots\text{HF}$ ,  $\text{H}_2\text{O}\cdots\text{HOH}$ , and  $\text{H}_3\text{N}\cdots\text{HNH}_2$ , in which the hydrogen bonds are denoted by dots. [\[link\]](#) illustrates hydrogen bonding between water molecules.



Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 ( $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{SbH}_3$ ), group 16 hydrides ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$ ), and group 17 hydrides ( $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$ ). The boiling points of the heaviest three hydrides for each group are plotted in [\[link\]](#). As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

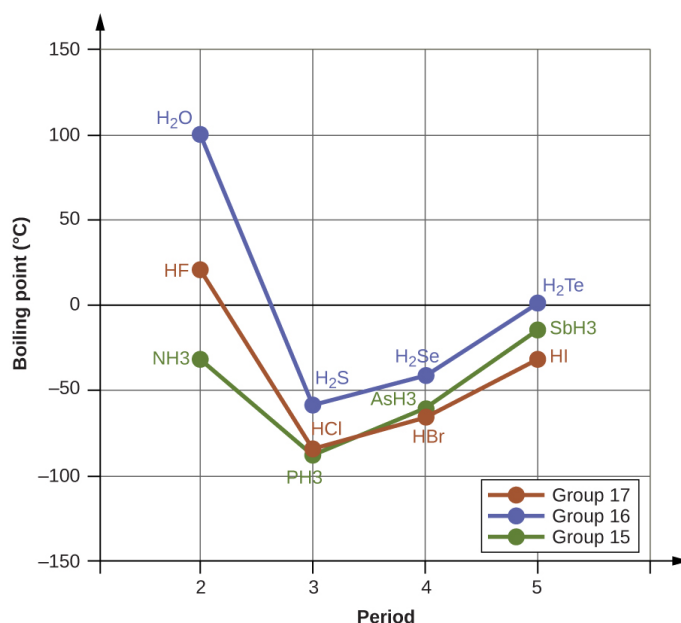


For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect  $\text{NH}_3$  to boil at about  $-120\text{ }^\circ\text{C}$ ,  $\text{H}_2\text{O}$  to boil at about  $-80\text{ }^\circ\text{C}$ , and  $\text{HF}$  to boil at about  $-110\text{ }^\circ\text{C}$ . However, when we measure the boiling points for these compounds, we find that they are dramatically



higher than the trends would predict, as shown in [\[link\]](#). The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.



In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

### Example:

#### Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether ( $\text{CH}_3\text{OCH}_3$ ), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), and propane ( $\text{CH}_3\text{CH}_2\text{CH}_3$ ). Their boiling points, not necessarily in order, are  $-42.1^\circ\text{C}$ ,  $-24.8^\circ\text{C}$ , and  $78.4^\circ\text{C}$ . Match each compound with its boiling point. Explain your reasoning.

#### Solution

The VSEPR-predicted shapes of  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , and  $\text{CH}_3\text{CH}_2\text{CH}_3$  are similar, as are their molar masses (46 g/mol, 46 g/mol,

and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since  $\text{CH}_3\text{CH}_2\text{CH}_3$  is nonpolar, it may exhibit *only* dispersion forces. Because  $\text{CH}_3\text{OCH}_3$  is polar, it will also experience dipole-dipole attractions. Finally,  $\text{CH}_3\text{CH}_2\text{OH}$  has an  $-\text{OH}$  group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is  $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CH}_2\text{OH}$ . The boiling point of propane is  $-42.1\text{ }^\circ\text{C}$ , the boiling point of dimethylether is  $-24.8\text{ }^\circ\text{C}$ , and the boiling point of ethanol is  $78.5\text{ }^\circ\text{C}$ .

### Check Your Learning

Ethane ( $\text{CH}_3\text{CH}_3$ ) has a melting point of  $-183\text{ }^\circ\text{C}$  and a boiling point of  $-89\text{ }^\circ\text{C}$ . Predict the melting and boiling points for methylamine ( $\text{CH}_3\text{NH}_2$ ). Explain your reasoning.

### Note:

#### Answer:

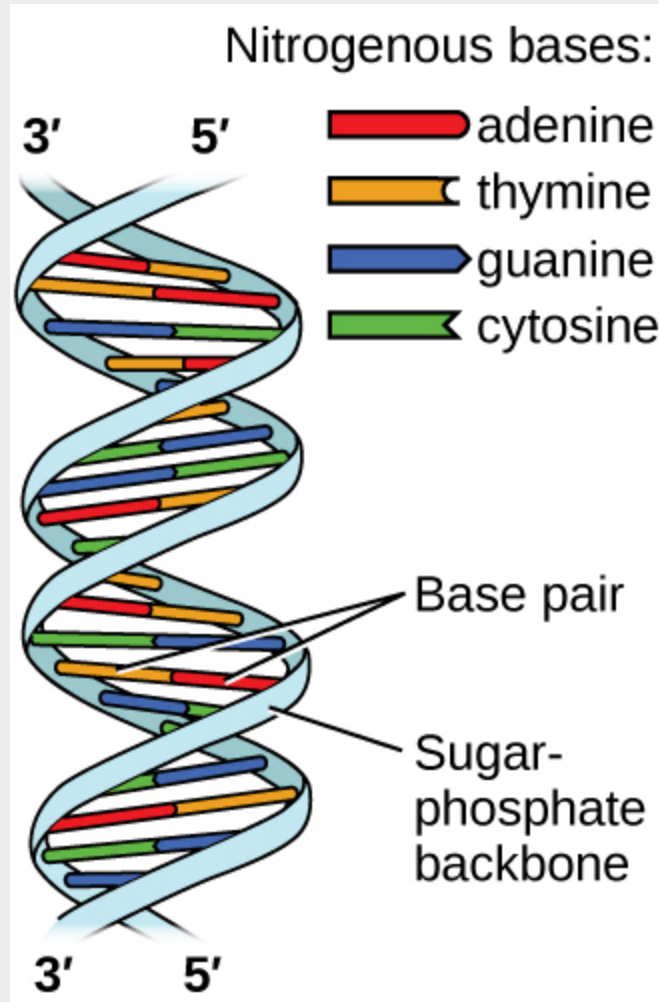
The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane.  $\text{CH}_3\text{CH}_3$  and  $\text{CH}_3\text{NH}_2$  are similar in size and mass, but methylamine possesses an  $-\text{NH}$  group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of  $-93\text{ }^\circ\text{C}$  and a boiling point of  $-6\text{ }^\circ\text{C}$ .

### Note:

#### Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of

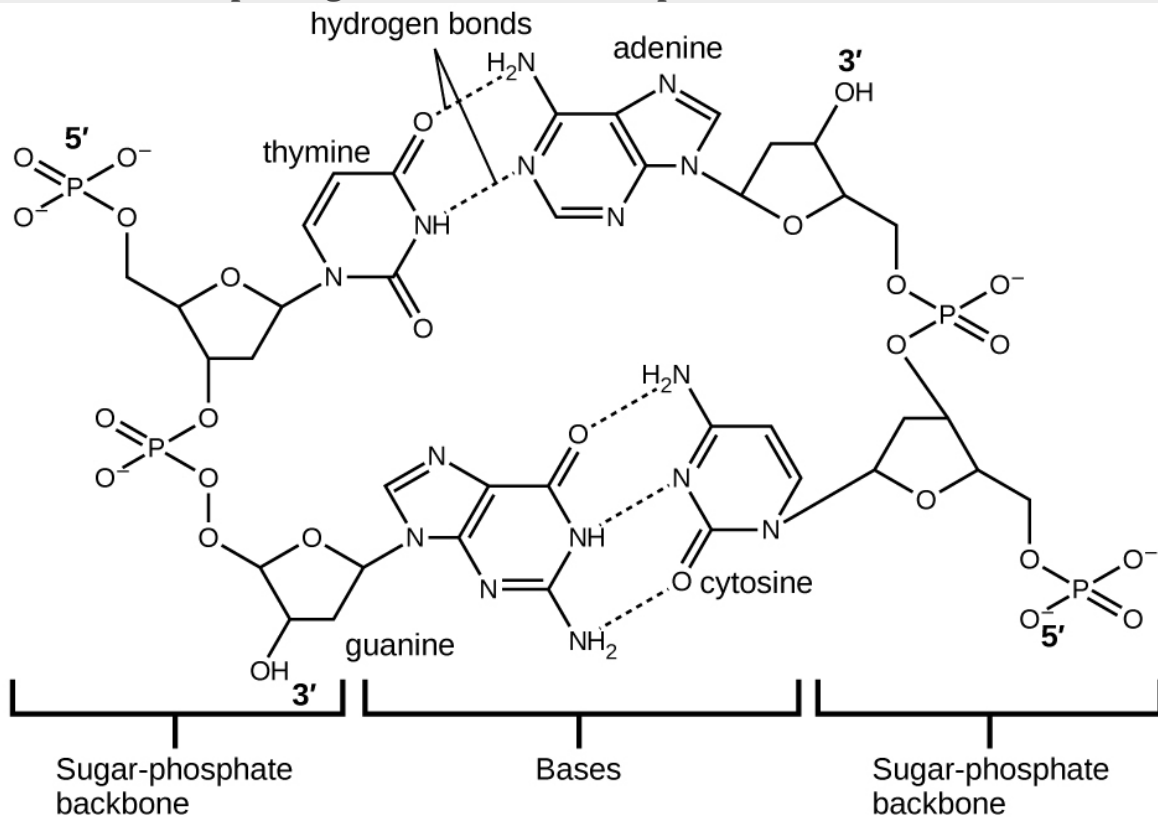
repeating nucleotides, which form its well-known double helical structure, as shown in [\[link\]](#).



Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-

ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure [\[link\]](#).



The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

## Key Concepts and Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one polar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

In terms of their bulk properties, how do liquids and solids differ?  
How are they similar?

---

#### Solution:

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

### Exercise:

**Problem:**

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

**Exercise:****Problem:**

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

---

**Solution:**

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

**Exercise:****Problem:**

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

**Exercise:****Problem:**

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

---

**Solution:**

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

**Exercise:**

**Problem:**

Open the [PhET States of Matter Simulation](#) to answer the following questions:

- (a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
- (b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
- (c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

**Exercise:**

**Problem:** Define the following and give an example of each:

- (a) dispersion force
- (b) dipole-dipole attraction
- (c) hydrogen bond

---

**Solution:**

- (a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon

or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (e.g., Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (e.g., ICl molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (e.g.,

**Exercise:**

**Problem:**

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

**Exercise:**

**Problem:**

Why do the boiling points of the noble gases increase in the order  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ ?

---

**Solution:**

The London forces typically increase as the number of electrons increase.

**Exercise:**

**Problem:**

Neon and HF have approximately the same molecular masses.



- (a) Explain why the boiling points of Neon and HF differ.
- (b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

**Exercise:**

**Problem:**

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

- (a) HCl, H<sub>2</sub>O, SiH<sub>4</sub>
- (b) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>
- (c) CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>
- (d) O<sub>2</sub>, NO, N<sub>2</sub>

---

**Solution:**

(a) SiH<sub>4</sub> < HCl < H<sub>2</sub>O; (b) F<sub>2</sub> < Cl<sub>2</sub> < Br<sub>2</sub>; (c) CH<sub>4</sub> < C<sub>2</sub>H<sub>6</sub> < C<sub>3</sub>H<sub>8</sub>; (d) N<sub>2</sub> < O<sub>2</sub> < NO

**Exercise:**

**Problem:**

The molecular mass of butanol, C<sub>4</sub>H<sub>9</sub>OH, is 74.14; that of ethylene glycol, CH<sub>2</sub>(OH)CH<sub>2</sub>OH, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

**Exercise:**

**Problem:**

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*-butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.

---

**Solution:**

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction, therefore, is stronger, leading to a higher boiling point.

**Exercise:****Problem:**

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

**Exercise:****Problem:**

The melting point of H<sub>2</sub>O(s) is 0 °C. Would you expect the melting point of H<sub>2</sub>S(s) to be -85 °C, 0 °C, or 185 °C? Explain your answer.

---

**Solution:**

-85 °C. Water has stronger hydrogen bonds, so it melts at a higher temperature.

**Exercise:****Problem:**

Silane (SiH<sub>4</sub>), phosphine (PH<sub>3</sub>), and hydrogen sulfide (H<sub>2</sub>S) melt at -185 °C, -133 °C, and -85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

**Exercise:****Problem:**

Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

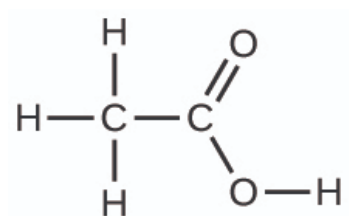
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**Solution:**

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

**Exercise:****Problem:**

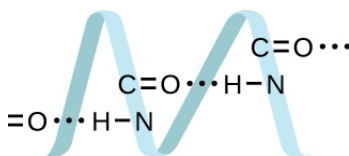
Under certain conditions, molecules of acetic acid,  $\text{CH}_3\text{COOH}$ , form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two  $\text{CH}_3\text{COOH}$  molecules are held together, and stating the type of IMF that is responsible.

**Exercise:****Problem:**

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



**Solution:**

H-bonding is the principle IMF holding the protein strands together.  
The H-bonding is between the                      and

**Exercise:****Problem:**

The density of liquid  $\text{NH}_3$  is 0.64 g/mL; the density of gaseous  $\text{NH}_3$  at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

**Exercise:****Problem:**

Identify the intermolecular forces present in the following solids:

(a)  $\text{CH}_3\text{CH}_2\text{OH}$

(b)  $\text{CH}_3\text{CH}_2\text{CH}_3$

(c)  $\text{CH}_3\text{CH}_2\text{Cl}$

---

**Solution:**

- (a) hydrogen bonding, dipole-dipole attraction, and dispersion forces;  
(b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

**Glossary**

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

## Properties of Liquids

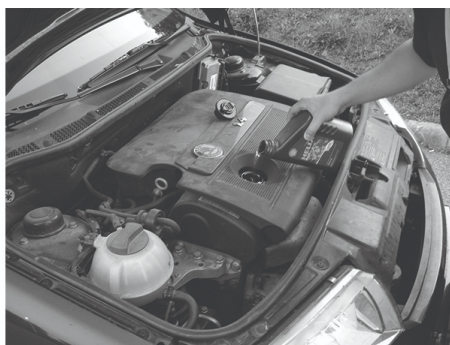
By the end of this section, you will be able to:

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in [\[link\]](#), have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).



(a)



(b)

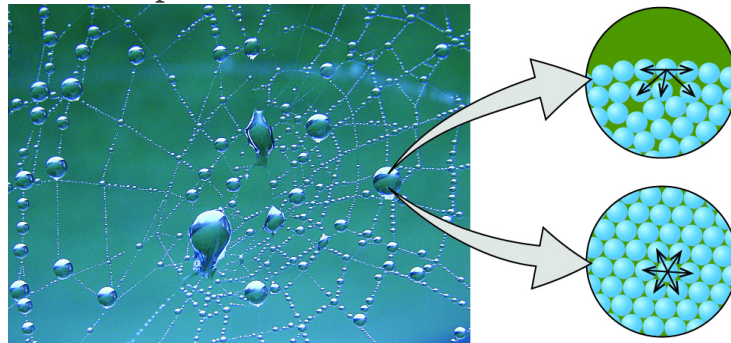
(a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As [\[link\]](#) shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Viscosities of Common Substances at 25 °C		
Substance	Formula	Viscosity (mPa·s)
water	H <sub>2</sub> O	0.890
mercury	Hg	1.526
ethanol	C <sub>2</sub> H <sub>5</sub> OH	1.074
octane	C <sub>8</sub> H <sub>18</sub>	0.508
ethylene glycol	CH <sub>2</sub> (OH)CH <sub>2</sub> (OH)	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of **cohesive forces**. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the

unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in [\[link\]](#), because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.



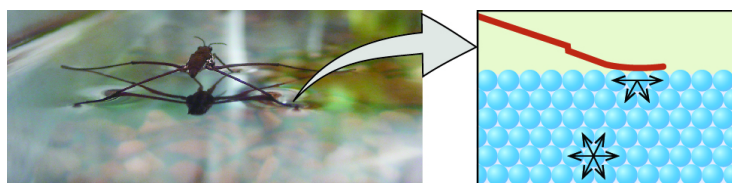
Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by “OliBac”/Flickr)

**Surface tension** is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in [\[link\]](#). Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively “tough skin” that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in [\[link\]](#), even though they are denser than



water, move on its surface because they are supported by the surface tension.

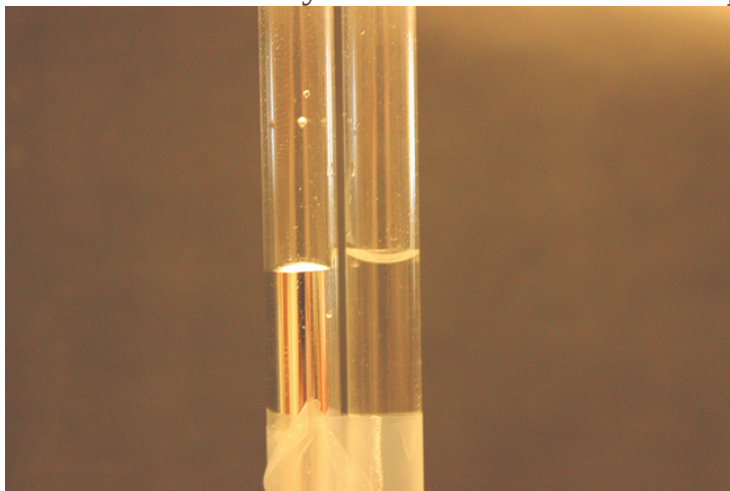
Surface Tensions of Common Substances at 25 °C		
Substance	Formula	Surface Tension (mN/m)
water	H <sub>2</sub> O	71.99
mercury	Hg	458.48
ethanol	C <sub>2</sub> H <sub>5</sub> OH	21.97
octane	C <sub>8</sub> H <sub>18</sub>	21.14
ethylene glycol	CH <sub>2</sub> (OH)CH <sub>2</sub> (OH)	47.99



Surface tension (right) prevents this insect, a “water strider,” from sinking into the water.

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some

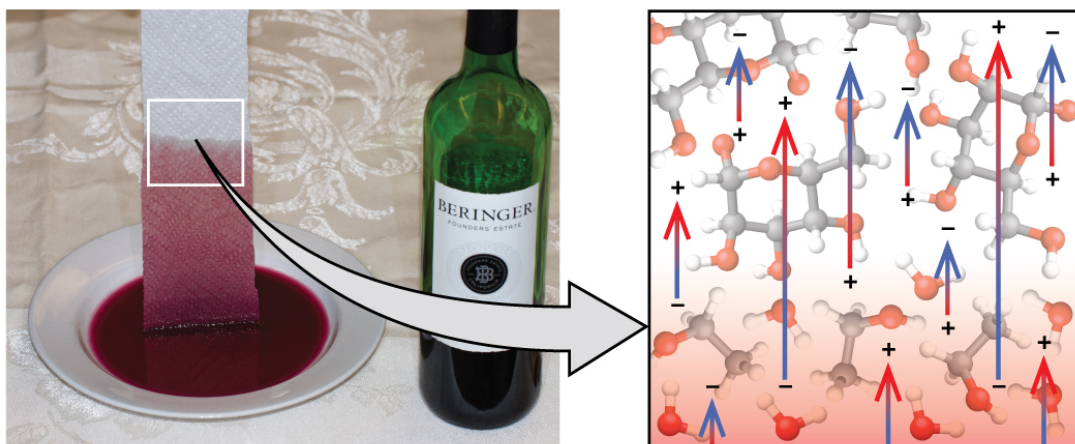
surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not “wet” the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop ([\[link\]](#)).



Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes.  
(credit: Mark Ott)

If you place one end of a paper towel in spilled wine, as shown in [\[link\]](#), the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary**

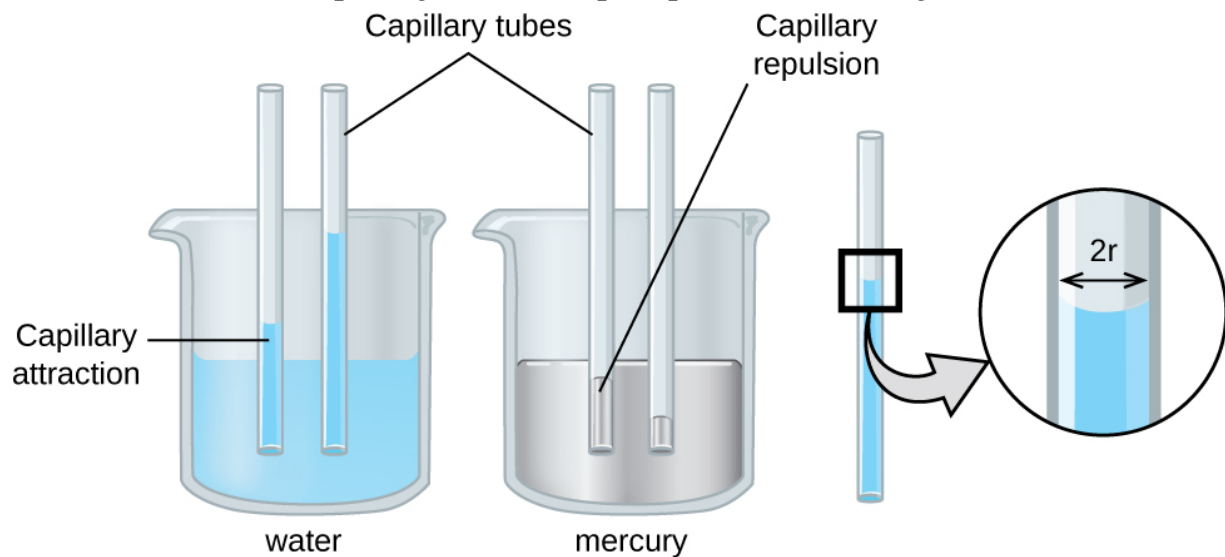
**action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.



Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the  $\text{-OH}$  groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many  $\text{-OH}$  groups. Water molecules are attracted to these  $\text{-OH}$  groups and form hydrogen bonds with them, which draws the  $\text{H}_2\text{O}$  molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in [\[link\]](#). If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.



Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

**Equation:**

---

In this equation,  $h$  is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube,  $T$  is the surface tension of the liquid,  $\theta$  is the contact angle between the liquid and the tube,  $r$  is the radius of the tube,  $\rho$  is the density of the liquid, and  $g$  is the acceleration due to gravity,  $9.8 \text{ m/s}^2$ . When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of  $0^\circ$ . This is the situation for water rising in a glass tube.

**Example:****Capillary Rise**

At  $25^\circ\text{C}$ , how high will water rise in a glass capillary tube with an inner diameter of  $0.25 \text{ mm}$ ?

For water,  $T = 71.99 \text{ mN/m}$  and  $\rho = 1.0 \text{ g/cm}^3$ .

**Solution**

The liquid will rise to a height  $h$  given by: \_\_\_\_\_

The Newton is defined as a  $\text{kg m/s}^2$ , and so the provided surface tension is equivalent to  $0.07199 \text{ kg/s}^2$ . The provided density must be converted into units that will cancel appropriately:  $\rho = 1000 \text{ kg/m}^3$ . The diameter of the tube in meters is  $0.00025 \text{ m}$ , so the radius is  $0.000125 \text{ m}$ . For a glass tube immersed in water, the contact angle is  $\theta = 0^\circ$ , so  $\cos \theta = 1$ . Finally, acceleration due to gravity on the earth is  $g = 9.8 \text{ m/s}^2$ . Substituting these values into the equation, and cancelling units, we have:

**Equation:**

---

**Check Your Learning**

Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

**Note:**

**Answer:**

diameter = 0.36 mm

**Note:**

### Biomedical Applications of Capillary Action

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in [\[link\]](#). When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.



Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

## Key Concepts and Summary

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

## Key Equations

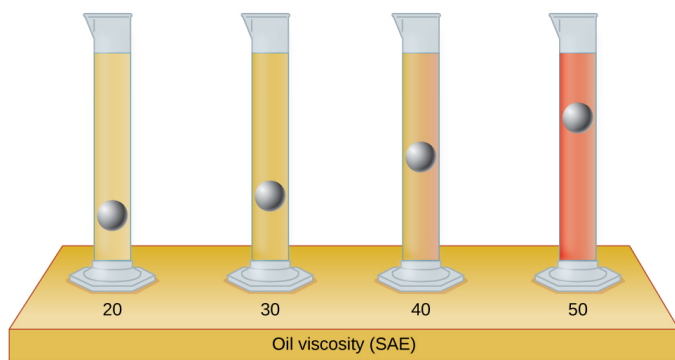
## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.

Rank the motor oils in order of increasing viscosity, and explain your reasoning:

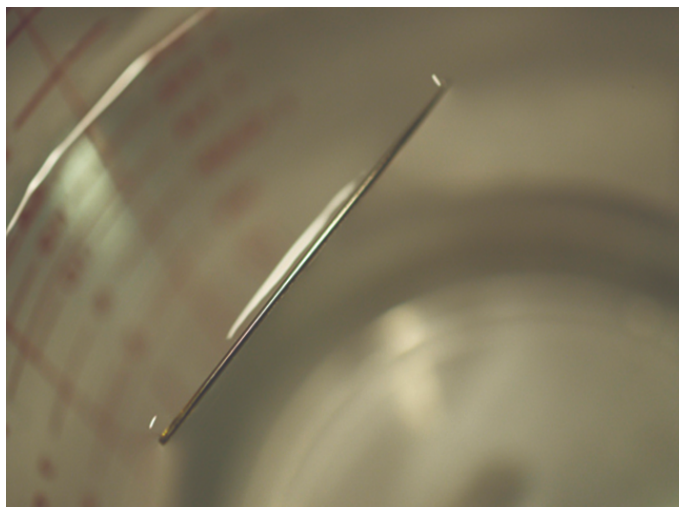


### Exercise:

#### Problem:

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible.





(credit: Cory Zanker)

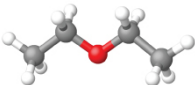
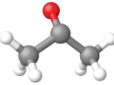
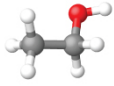
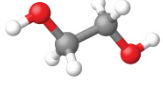
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**Solution:**

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or paper clip if gently placed on the water.

**Exercise:****Problem:**

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$		17	0.22
acetone $\text{CH}_3\text{COCH}_3$		23	0.31
ethanol $\text{C}_2\text{H}_5\text{OH}$		22	1.07
ethylene glycol $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$		48	16.1

(a) Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.

(b) Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

### Exercise:

#### Problem:

You may have heard someone use the figure of speech “slower than molasses in winter” to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

#### Solution:

Temperature has an effect on intermolecular forces: The higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid. The lower the temperature, the less the intermolecular forces are overcome, and so the less viscous the liquid.

### Exercise:

**Problem:**

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

**Exercise:****Problem:**

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

---

**Solution:**

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

**Exercise:**

**Problem:**

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to [\[link\]](#) for the required information.

**Exercise:**

**Problem:**

Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

---

**Solution:**

1.7  $\times 10^{-4}$  m

## Glossary

adhesive force

force of attraction between molecules of different chemical identities

capillary action

flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

cohesive force

force of attraction between identical molecules

surface tension

energy required to increase the area, or length, of a liquid surface by a given amount

viscosity

measure of a liquid's resistance to flow

## Phase Transitions

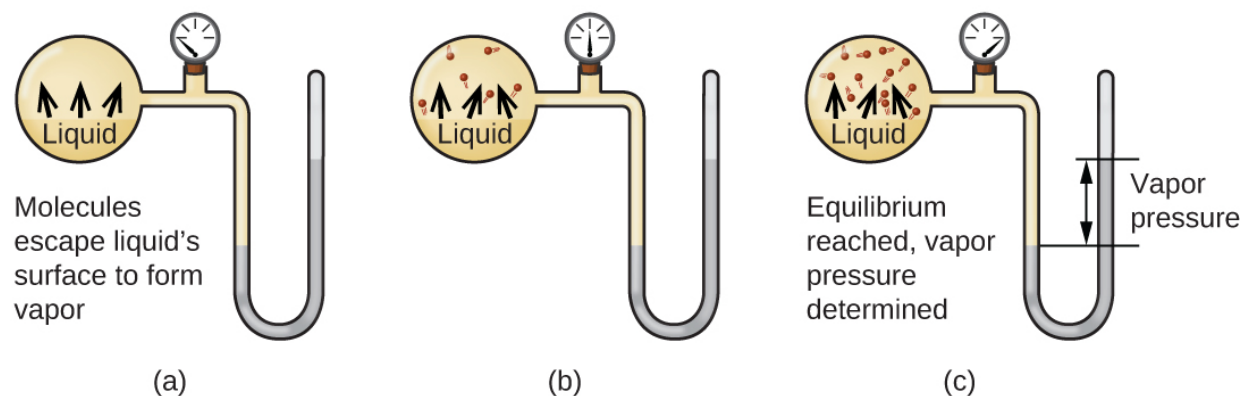
By the end of this section, you will be able to:

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

## Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a **dynamic equilibrium**, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapor pressure** (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in [\[link\]](#), and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.



In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring “recapture”

of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

**Example:**  
**Explaining Vapor Pressure in Terms of IMFs**  
 Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:

$\begin{array}{c} \text{OH} \\   \\ \text{H}_3\text{C}-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{HO} \quad \text{OH} \\   \quad   \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$	$\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$	and $\text{H}-\text{O}-\text{H}$
ethanol	ethylene glycol	diethyl ether	water

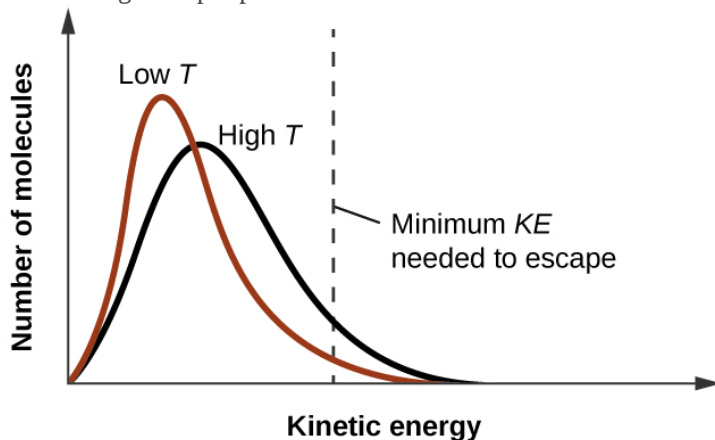
**Solution**  
 Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two –OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

**Check Your Learning**  
 At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH <sub>3</sub> OH	ethanol C <sub>2</sub> H <sub>5</sub> OH	propanol C <sub>3</sub> H <sub>7</sub> OH	butanol C <sub>4</sub> H <sub>9</sub> OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

**Note:**  
**Answer:**  
 All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:  
 $P_{\text{methanol}} > P_{\text{ethanol}} > P_{\text{propanol}} > P_{\text{butanol}}$

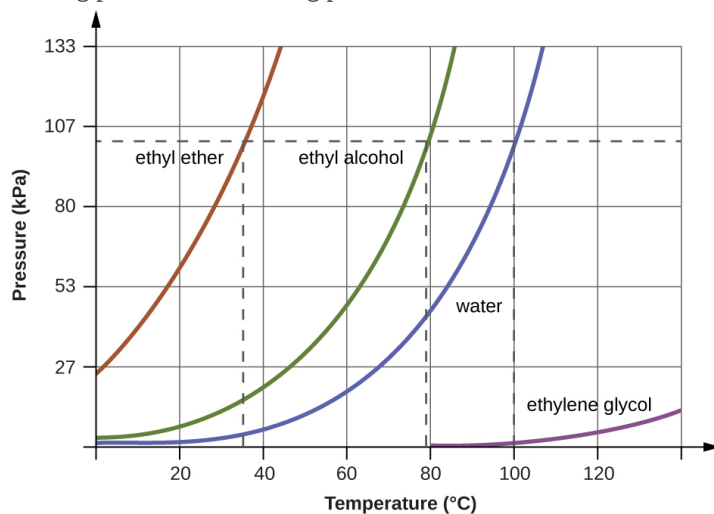
As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in [\[link\]](#). The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.



Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

## Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The **boiling point** of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). [\[link\]](#) shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.





The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

**Example:**

**A Boiling Point at Reduced Pressure**

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in [\[link\]](#) to determine the boiling point of water at this elevation.

**Solution**

The graph of the vapor pressure of water versus temperature in [\[link\]](#) indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

**Check Your Learning**

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use [\[link\]](#) to determine the approximate atmospheric pressure at the camp.

**Note:**

**Answer:**

Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the **Clausius-Clapeyron equation**:

**Equation:**

$$P = Ae^{-\Delta H_{\text{vap}}/RT}$$

where  $\Delta H_{\text{vap}}$  is the enthalpy of vaporization for the liquid,  $R$  is the gas constant, and  $A$  is a constant whose value depends on the chemical identity of the substance. Temperature  $T$  must be in Kelvin in this equation. This equation is often rearranged into logarithmic form to yield the linear equation:

**Equation:**

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the example exercises that follow. If at temperature  $T_1$ , the vapor pressure is  $P_1$ , and at temperature  $T_2$ , the vapor pressure is  $P_2$ , the corresponding linear equations are:

**Equation:**

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + \ln A \quad \text{and} \quad \ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + \ln A$$

Since the constant,  $A$ , is the same, these two equations may be rearranged to isolate  $\ln A$  and then set them equal to one another:

**Equation:**

$$\ln P_1 + \frac{\Delta H_{\text{vap}}}{RT_1} = \ln P_2 + \frac{\Delta H_{\text{vap}}}{RT_2}$$

which can be combined into:

**Equation:**

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

**Example:**

#### Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

**Solution**

The enthalpy of vaporization,  $\Delta H_{\text{vap}}$ , can be determined by using the Clausius-Clapeyron equation:

**Equation:**

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since we have two vapor pressure-temperature values ( $T_1 = 34.0\text{ °C} = 307.2\text{ K}$ ,  $P_1 = 10.0\text{ kPa}$  and  $T_2 = 98.8\text{ °C} = 372.0\text{ K}$ ,  $P_2 = 100\text{ kPa}$ ), we can substitute them into this equation and solve for  $\Delta H_{\text{vap}}$ . Rearranging the Clausius-Clapeyron equation and solving for  $\Delta H_{\text{vap}}$  yields:

**Equation:**

$$\Delta H_{\text{vap}} = \frac{R \cdot \ln \left( \frac{P_2}{P_1} \right)}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.3145\text{ J/mol}\cdot\text{K}) \cdot \ln \left( \frac{100\text{ kPa}}{10.0\text{ kPa}} \right)}{\left( \frac{1}{307.2\text{ K}} - \frac{1}{372.0\text{ K}} \right)} = 33,800\text{ J/mol} = 33.8\text{ kJ/mol}$$

Note that the pressure can be in any units, so long as they agree for both  $P$  values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

#### Check Your Learning

At 20.0 °C, the vapor pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapor pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

**Note:**

**Answer:**

41,360 J/mol or 41.4 kJ/mol

**Example:**

#### Estimating Temperature (or Vapor Pressure)

For benzene (C<sub>6</sub>H<sub>6</sub>), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

**Solution**

If the temperature and vapor pressure are known at one point, along with the enthalpy of vaporization,  $\Delta H_{\text{vap}}$ , then the temperature that corresponds to a different vapor pressure (or the vapor pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation:

**Equation:**

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since the normal boiling point is the temperature at which the vapor pressure equals atmospheric pressure at sea level, we know one vapor pressure-temperature value ( $T_1 = 80.1 \text{ °C} = 353.3 \text{ K}$ ,  $P_1 = 101.3 \text{ kPa}$ ,  $\Delta H_{\text{vap}} = 30.8 \text{ kJ/mol}$ ) and want to find the temperature ( $T_2$ ) that corresponds to vapor pressure  $P_2 = 83.4 \text{ kPa}$ . We can substitute these values into the Clausius-Clapeyron equation and then solve for  $T_2$ . Rearranging the Clausius-Clapeyron equation and solving for  $T_2$  yields:

**Equation:**

$$T_2 = \left( \frac{-R \cdot \ln \left( \frac{P_2}{P_1} \right)}{\Delta H_{\text{vap}}} + \frac{1}{T_1} \right)^{-1} = \left( \frac{-(8.3145 \text{ J/mol}\cdot\text{K}) \cdot \ln \left( \frac{83.4 \text{ kPa}}{101.3 \text{ kPa}} \right)}{30,800 \text{ J/mol}} + \frac{1}{353.3 \text{ K}} \right)^{-1} = 346.9 \text{ K or } 73.5 \text{ °C}$$

**Check Your Learning**

For acetone (CH<sub>3</sub>)<sub>2</sub>CO, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapor pressure of acetone at 25.0 °C?

**Note:**

**Answer:**

30.1 kPa

## Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization,  $\Delta H_{\text{vap}}$ . For example, the vaporization of water at standard temperature is represented by:

**Equation:**



As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

**Equation:**



**Example:****Using Enthalpy of Vaporization**

One way our body is cooled is by evaporation of the water in sweat ([link](#)). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at  $T = 37\text{ }^{\circ}\text{C}$  (normal body temperature);  $\Delta H_{\text{vap}} = 43.46\text{ kJ/mol}$  at  $37\text{ }^{\circ}\text{C}$ .



Evaporation of sweat helps cool the body. (credit: “Kullez”/Flickr)

**Solution**

We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

**Equation:**

$$1.5\text{ L} \times \frac{1000\text{ g}}{1\text{ L}} \times \frac{1\text{ mol}}{18\text{ g}} \times \frac{43.46\text{ kJ}}{1\text{ mol}} = 3.6 \times 10^3\text{ kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

**Check Your Learning**

How much heat is required to evaporate 100.0 g of liquid ammonia,  $\text{NH}_3$ , at its boiling point if its enthalpy of vaporization is  $4.8\text{ kJ/mol}$ ?

**Note:****Answer:**

28 kJ

**Melting and Freezing**

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid

state, or **melting**. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid ([link](#)).



(a) This beaker of ice has a temperature of  $-12.0\text{ }^{\circ}\text{C}$ . (b) After 10 minutes the ice has absorbed enough heat from the air to warm to  $0\text{ }^{\circ}\text{C}$ . A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still  $0\text{ }^{\circ}\text{C}$ . The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to  $22.2\text{ }^{\circ}\text{C}$ . (credit: modification of work by Mark Ott)

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the **freezing point** of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion,  $\Delta H_{\text{fus}}$  of the substance. The enthalpy of fusion of ice is  $6.0\text{ kJ/mol}$  at  $0\text{ }^{\circ}\text{C}$ . Fusion (melting) is an endothermic process:

**Equation:**



The reciprocal process, freezing, is an exothermic process whose enthalpy change is  $-6.0\text{ kJ/mol}$  at  $0\text{ }^{\circ}\text{C}$ :

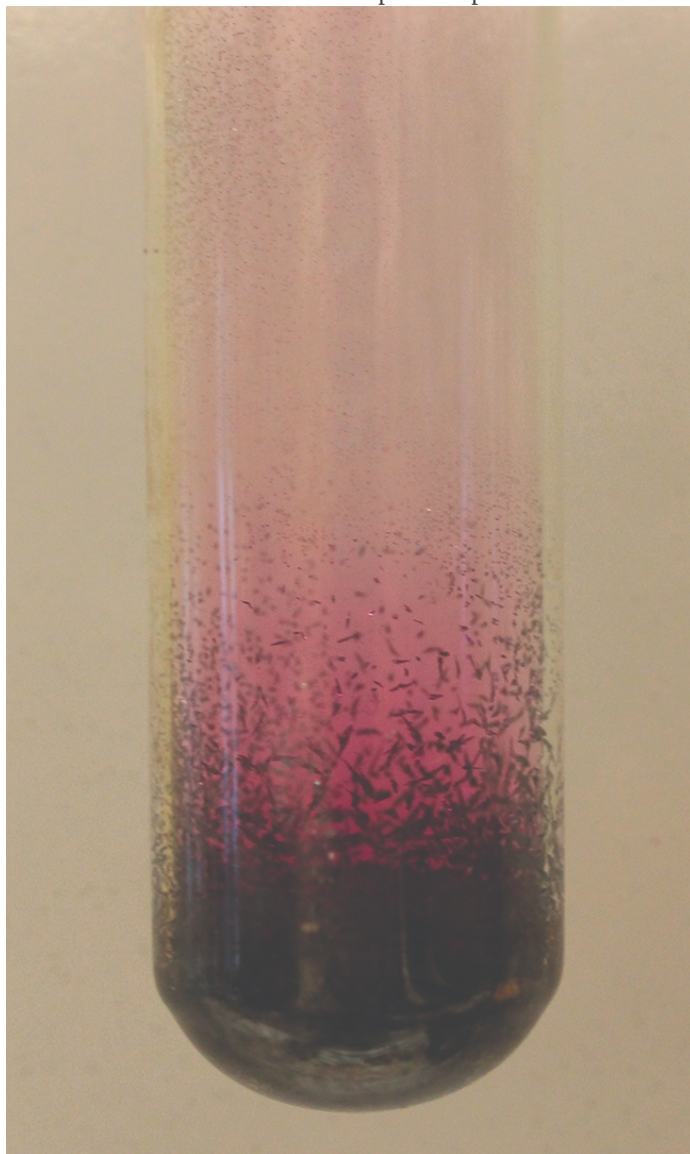
**Equation:**



## Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid  $\text{CO}_2$ ) sublimates, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high

altitudes. When solid iodine is warmed, the solid sublimates and a vivid purple vapor forms ([link](#)). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation,  $\Delta H_{\text{sub}}$ , is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

**Equation:**



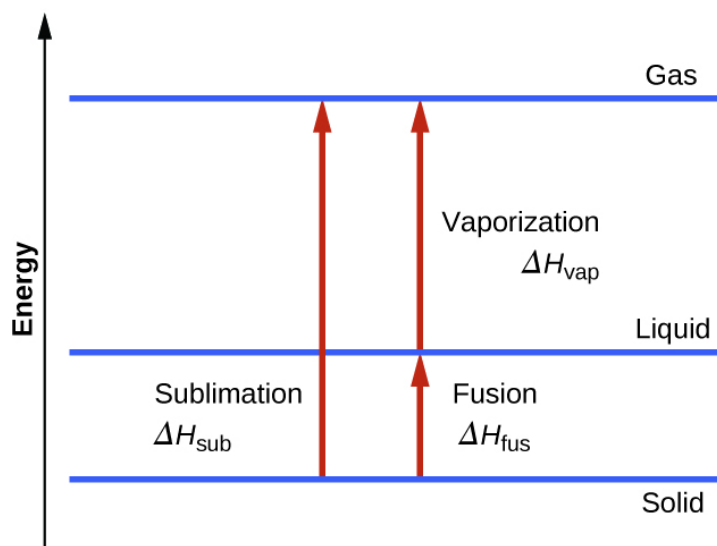
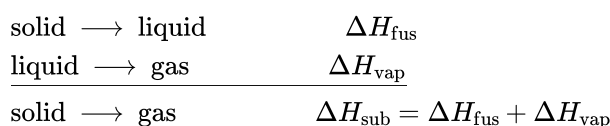
Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

**Equation:**



Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in [\[link\]](#). For example:

**Equation:**



For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

## Heating and Cooling Curves

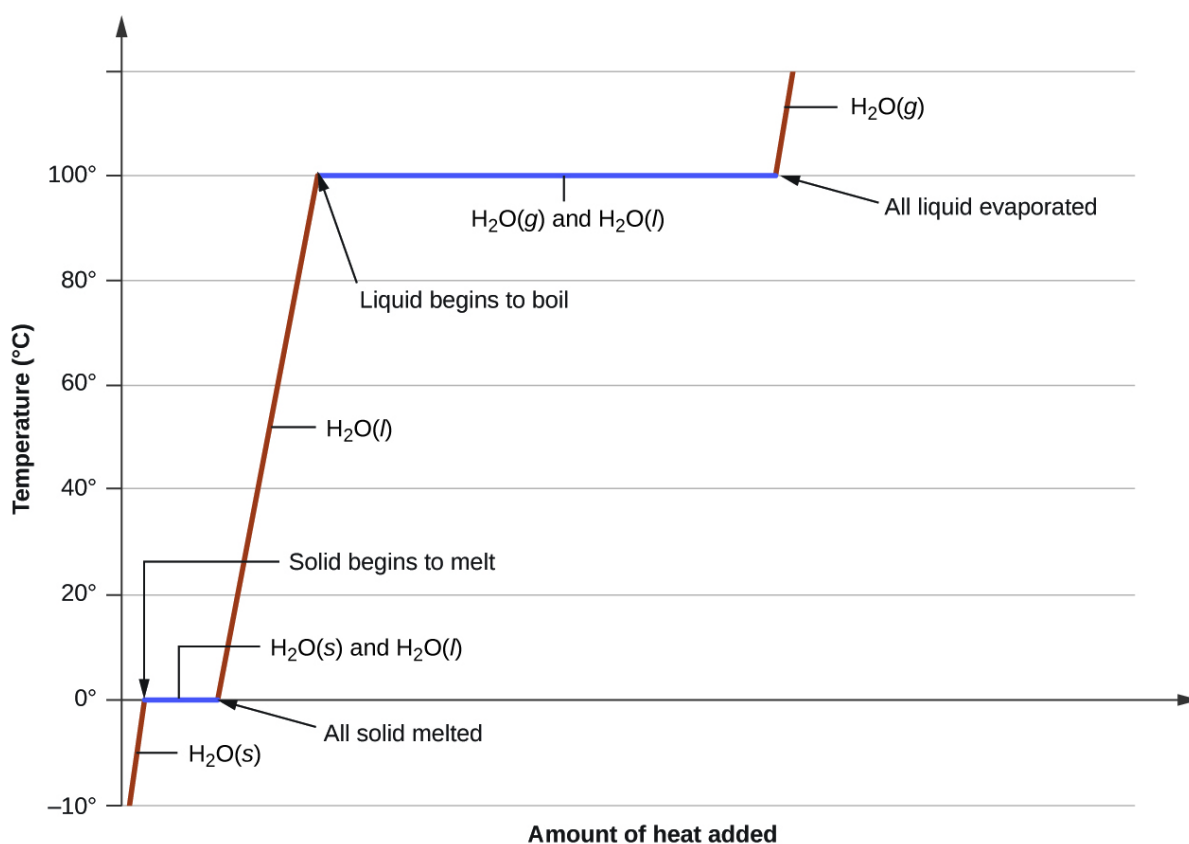
In the chapter on thermochemistry, the relation between the amount of heat absorbed or released by a substance,  $q$ , and its accompanying temperature change,  $\Delta T$ , was introduced:

**Equation:**

$$q = mc\Delta T$$

where  $m$  is the mass of the substance and  $c$  is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. [\[link\]](#) shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.



A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

**Example:****Total Heat Needed to Change Temperature and Phase for a Substance**

How much heat is required to convert 135 g of ice at  $-15^{\circ}\text{C}$  into water vapor at  $120^{\circ}\text{C}$ ?

**Solution**



The transition described involves the following steps:

1. Heat ice from  $-15\text{ }^{\circ}\text{C}$  to  $0\text{ }^{\circ}\text{C}$
2. Melt ice
3. Heat water from  $0\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$
4. Boil water
5. Heat steam from  $100\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$

The heat needed to change the temperature of a given substance (with no change in phase) is:  $q = m \times c \times \Delta T$  (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by  $q = n \times \Delta H$ .

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

**Equation:**

$$q_{\text{total}} = (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}}$$

**Equation:**

$$\begin{aligned} &= (135\text{ g} \cdot 2.09\text{ J/g} \cdot ^{\circ}\text{C} \cdot 15^{\circ}\text{C}) + \left(135 \cdot \frac{1\text{ mol}}{18.02\text{ g}} \cdot 6.01\text{ kJ/mol}\right) \\ &+ (135\text{ g} \cdot 4.18\text{ J/g} \cdot ^{\circ}\text{C} \cdot 100^{\circ}\text{C}) + \left(135\text{ g} \cdot \frac{1\text{ mol}}{18.02\text{ g}} \cdot 40.67\text{ kJ/mol}\right) \\ &+ (135\text{ g} \cdot 1.84\text{ J/g} \cdot ^{\circ}\text{C} \cdot 20^{\circ}\text{C}) \\ &= 4230\text{ J} + 45.0\text{ kJ} + 56,500\text{ J} + 305\text{ kJ} + 4970\text{ J} \end{aligned}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

**Equation:**

$$= 4.23\text{ kJ} + 45.0\text{ kJ} + 56.5\text{ kJ} + 305\text{ kJ} + 4.97\text{ kJ} = 416\text{ kJ}$$

### Check Your Learning

What is the total amount of heat released when 94.0 g water at  $80.0\text{ }^{\circ}\text{C}$  cools to form ice at  $-30.0\text{ }^{\circ}\text{C}$ ?

**Note:**

**Answer:**

68.7 kJ

## Key Concepts and Summary

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

## Key Equations

$$P = Ae^{-\Delta H_{\text{vap}}/RT}$$

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$$

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

### Exercise:

#### Problem:

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

#### Solution:

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

### Exercise:

#### Problem:

What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

### Exercise:

#### Problem:

Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

#### Solution:

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

### Exercise:

#### Problem:

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

### Exercise:

**Problem:** What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

#### Solution:

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

**Exercise:**

**Problem:** What is the relationship between the intermolecular forces in a solid and its melting temperature?

**Exercise:**

**Problem:** Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

---

**Solution:**

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

**Exercise:**

**Problem:**

Carbon tetrachloride,  $\text{CCl}_4$ , was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At  $57.8^\circ\text{C}$ , the vapor pressure of  $\text{CCl}_4$  is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for  $\text{CCl}_4$ .

**Exercise:**

**Problem:** When is the boiling point of a liquid equal to its normal boiling point?

---

**Solution:**

They are equal when the pressure of gas above the liquid is exactly 1 atm.

**Exercise:**

**Problem:** How does the boiling of a liquid differ from its evaporation?

**Exercise:**

**Problem:**

Use the information in [\[link\]](#) to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

---

**Solution:**

approximately  $95^\circ\text{C}$

**Exercise:**

**Problem:**

A syringe at a temperature of  $20^\circ\text{C}$  is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

**Exercise:**

**Problem:** Explain the following observations:

(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).

(b) Perspiring is a mechanism for cooling the body.

---

**Solution:**

(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

**Exercise:**

**Problem:** The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

**Exercise:****Problem:**

Explain why the molar enthalpies of vaporization of the following substances increase in the order  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8$ , even though the type of IMF (dispersion) is the same.

---

**Solution:**

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

**Exercise:****Problem:**

Explain why the enthalpies of vaporization of the following substances increase in the order  $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O}$ , even though all three substances have approximately the same molar mass.

**Exercise:****Problem:**

The enthalpy of vaporization of  $\text{CO}_2(l)$  is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of  $\text{CS}_2(l)$  to be 28 kJ/mol, 9.8 kJ/mol, or  $-8.4$  kJ/mol? Discuss the plausibility of each of these answers.

---

**Solution:**

The boiling point of  $\text{CS}_2$  is higher than that of  $\text{CO}_2$  partially because of the higher molecular weight of  $\text{CS}_2$ ; consequently, the attractive forces are stronger in  $\text{CS}_2$ . It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for  $\text{CO}_2$ . A value of 28 kJ/mol would seem reasonable. A value of  $-8.4$  kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

**Exercise:****Problem:**

The hydrogen fluoride molecule, HF, is more polar than a water molecule,  $\text{H}_2\text{O}$  (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

**Exercise:****Problem:**

Ethyl chloride (boiling point,  $13^\circ\text{C}$ ) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

---

**Solution:**

The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

**Exercise:**

**Problem:** Which contains the compounds listed correctly in order of increasing boiling points?

- (a)  $\text{N}_2 < \text{CS}_2 < \text{H}_2\text{O} < \text{KCl}$
- (b)  $\text{H}_2\text{O} < \text{N}_2 < \text{CS}_2 < \text{KCl}$
- (c)  $\text{N}_2 < \text{KCl} < \text{CS}_2 < \text{H}_2\text{O}$
- (d)  $\text{CS}_2 < \text{N}_2 < \text{KCl} < \text{H}_2\text{O}$
- (e)  $\text{KCl} < \text{H}_2\text{O} < \text{CS}_2 < \text{N}_2$

**Exercise:**

**Problem:** How much heat is required to convert 422 g of liquid  $\text{H}_2\text{O}$  at  $23.5^\circ\text{C}$  into steam at  $150^\circ\text{C}$ ?

---

**Solution:**

1130 kJ

**Exercise:****Problem:**

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at  $3.8^\circ\text{C}$ , how much heat is needed to convert all of that water into sweat and then to vapor? (Note: Your body temperature is  $36.6^\circ\text{C}$ . For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

**Exercise:**

**Problem:** Titanium tetrachloride,  $\text{TiCl}_4$ , has a melting point of  $-23.2^\circ\text{C}$  and has a  $\Delta H_{\text{fusion}} = 9.37 \text{ kJ/mol}$ .

- (a) How much energy is required to melt 263.1 g  $\text{TiCl}_4$ ?
- (b) For  $\text{TiCl}_4$ , which will likely have the larger magnitude:  $\Delta H_{\text{fusion}}$  or  $\Delta H_{\text{vaporization}}$ ? Explain your reasoning.

---

**Solution:**

(a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

**Glossary**

boiling point

temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Clausius-Clapeyron equation

mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

condensation

change from a gaseous to a liquid state

deposition

change from a gaseous state directly to a solid state

dynamic equilibrium

state of a system in which reciprocal processes are occurring at equal rates

freezing

change from a liquid state to a solid state

freezing point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

melting

change from a solid state to a liquid state

melting point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

normal boiling point

temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

sublimation

change from solid state directly to gaseous state

vapor pressure

(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization

change from liquid state to gaseous state

## Introduction

class="introduction"

- The Dissolution Process
- Electrolytes
- Solubility
- Colligative Properties
- Colloids

Coral reefs, such as this one at the Palmyra Atoll National Wildlife Refuge, are vital to the ecosystem of earth's oceans. The health of coral reefs and all marine life depends on the specific chemical composition of the complex mixture known as seawater.

(credit: modification of work by "USFWS – Pacific Region"/Wikimedia Commons)



Coral reefs are home to about 25% of all marine species. They are being threatened by climate change, oceanic acidification, and water pollution, all of which change the composition of the solution known as seawater. Dissolved oxygen in seawater is critical for sea creatures, but as the oceans warm, oxygen becomes less soluble. As the concentration of carbon dioxide in the atmosphere increases, the concentration of carbon dioxide in the oceans increases, contributing to oceanic acidification. Coral reefs are particularly sensitive to the acidification of the ocean, since the exoskeletons of the coral polyps are soluble in acidic solutions. Humans contribute to the changing of seawater composition by allowing agricultural runoff and other forms of pollution to affect our oceans.

Solutions are crucial to the processes that sustain life and to many other processes involving chemical reactions. This chapter considers the nature of solutions and examines factors that determine whether a solution will form and what properties it may have. The properties of colloids—mixtures containing dispersed particles larger than the molecules and ions of typical solutions—are also discussed.



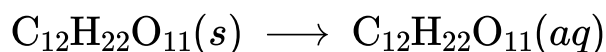
## The Dissolution Process

By the end of this section, you will be able to:

- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the *solvent*. The other components of the solution present in relatively lesser concentrations are called *solutes*. Sugar is a covalent solid composed of sucrose molecules,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

**Equation:**



The subscript “*aq*” in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to “settle out” over time.

Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , is an ionic compound composed of colorless potassium ions,  $\text{K}^+$ , and orange dichromate ions,  $\text{Cr}_2\text{O}_7^{2-}$ . When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture ([\[link\]](#)), as indicated in this equation:

**Equation:**



As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



When potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

**Note:**

Visit this [virtual lab](#) to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many **alloys** are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. [\[link\]](#) gives examples of several different solutions and the phases of the solutes and solvents.

---

Different Types of Solutions		
Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks <a href="#">[footnote]</a> If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in [\[link\]](#).
- The components of a solution are dispersed on a molecular scale; they consist of a mixture of separated solute particles (molecules, atoms, and/or ions) each closely surrounded by solvent species.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously (within limits determined by the *solubility* of the components, discussed in detail later in this chapter).

## The Formation of Solutions

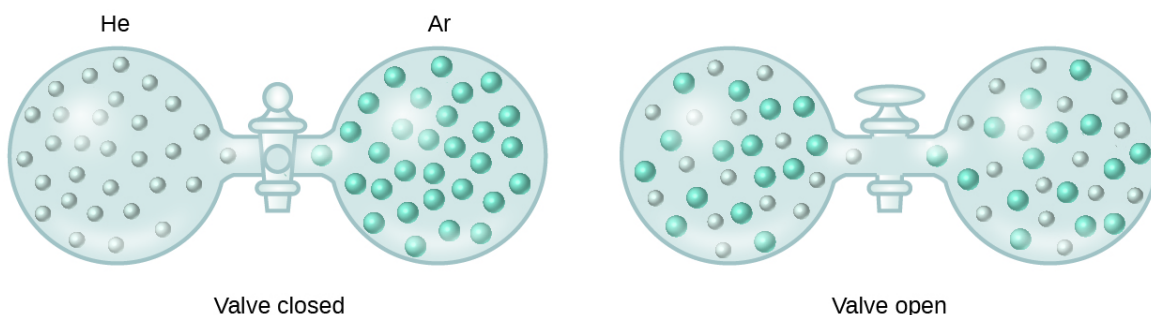
The formation of a solution is an example of a **spontaneous process**, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes a mixture is stirred to speed up the dissolution process, but this is not necessary; a homogeneous solution will form eventually. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increased dispersal of matter in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in matter dispersal always results when a solution forms from the uniform distribution of solute molecules throughout a solvent.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an **ideal solution**. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution ([\[link\]](#)). The formation of this solution clearly involves an increase in matter dispersal, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

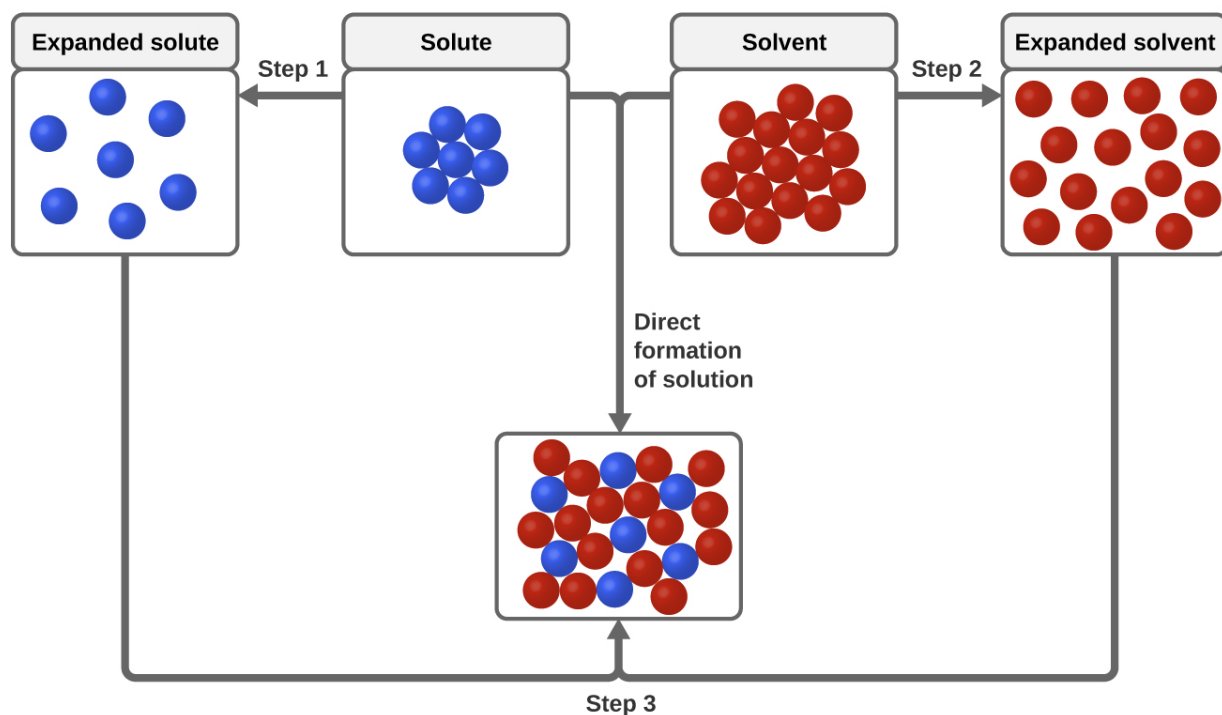


Samples of helium and argon spontaneously mix to give a solution.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) form ideal solutions, as do mixtures of the hydrocarbons pentane,  $\text{C}_5\text{H}_{12}$ , and hexane,  $\text{C}_6\text{H}_{14}$ . Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in [\[link\]](#) will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how increased matter dispersal alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in [\[link\]](#), the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to

as **solvation**). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.



This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

Consider the example of an ionic compound dissolving in water. Formation of the solution requires the electrostatic forces between the cations and anions of the compound (solute–solute) be overcome completely as attractive forces are established between these ions and water molecules (solute–solvent). Hydrogen bonding between a relatively small fraction of

the water molecules must also be overcome to accommodate any dissolved solute. If the solute's electrostatic forces are significantly greater than the solvation forces, the dissolution process is significantly endothermic and the compound may not dissolve to an appreciable extent. Calcium carbonate, the major component of coral reefs, is one example of such an “insoluble” ionic compound (see [\[link\]](#)). On the other hand, if the solvation forces are much stronger than the compound's electrostatic forces, the dissolution is significantly exothermic and the compound may be highly soluble. A common example of this type of ionic compound is sodium chloride, commonly known as table salt.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is one such example and is used to make instant cold packs for treating injuries like the one pictured in [\[link\]](#). A thin-walled plastic bag of water is sealed inside a larger bag with solid  $\text{NH}_4\text{NO}_3$ . When the smaller bag is broken, a solution of  $\text{NH}_4\text{NO}_3$  forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.



An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

**Note:**

Watch this brief [video](#) illustrating endothermic and exothermic dissolution processes.

## Key Concepts and Summary

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:**

How do solutions differ from compounds? From other mixtures?

---

**Solution:**



A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.

**Exercise:**

**Problem:**

Which of the principal characteristics of solutions are evident in the solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  shown in [\[link\]](#)?

**Exercise:**

**Problem:**

When  $\text{KNO}_3$  is dissolved in water, the resulting solution is significantly colder than the water was originally.

- (a) Is the dissolution of  $\text{KNO}_3$  an endothermic or an exothermic process?
- (b) What conclusions can you draw about the intermolecular attractions involved in the process?
- (c) Is the resulting solution an ideal solution?

---

**Solution:**

(a) The process is endothermic as the solution is consuming heat. (b) Attraction between the  $\text{K}^+$  and  $\text{NO}_3^-$  ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.

**Exercise:**

**Problem:** Give an example of each of the following types of solutions:

- (a) a gas in a liquid

(b) a gas in a gas

(c) a solid in a solid

**Exercise:**

**Problem:**

Indicate the most important types of intermolecular attractions in each of the following solutions:

(a) The solution in [\[link\]](#).

(b)  $\text{NO}(l)$  in  $\text{CO}(l)$

(c)  $\text{Cl}_2(g)$  in  $\text{Br}_2(l)$

(d)  $\text{HCl}(g)$  in benzene  $\text{C}_6\text{H}_6(l)$

(e) Methanol  $\text{CH}_3\text{OH}(l)$  in  $\text{H}_2\text{O}(l)$

---

**Solution:**

(a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding

**Exercise:**

**Problem:**

Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane ( $\text{C}_7\text{H}_{16}$ , nonpolar solvent):

(a) vegetable oil (nonpolar)

(b) isopropyl alcohol (polar)

(c) potassium bromide (ionic)

**Exercise:**

**Problem:**

Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

---

**Solution:**

Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.

**Exercise:****Problem:**

Solutions of hydrogen in palladium may be formed by exposing Pd metal to  $\text{H}_2$  gas. The concentration of hydrogen in the palladium depends on the pressure of  $\text{H}_2$  gas applied, but in a more complex fashion than can be described by Henry's law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal (solution density =  $10.8 \text{ g cm}^3$ ).

- (a) Determine the molarity of this solution.
- (b) Determine the molality of this solution.
- (c) Determine the percent by mass of hydrogen atoms in this solution.

**Glossary**

alloy

solid mixture of a metallic element and one or more additional elements

ideal solution

solution that forms with no accompanying energy change

solvation

exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

spontaneous process

physical or chemical change that occurs without the addition of energy from an external source

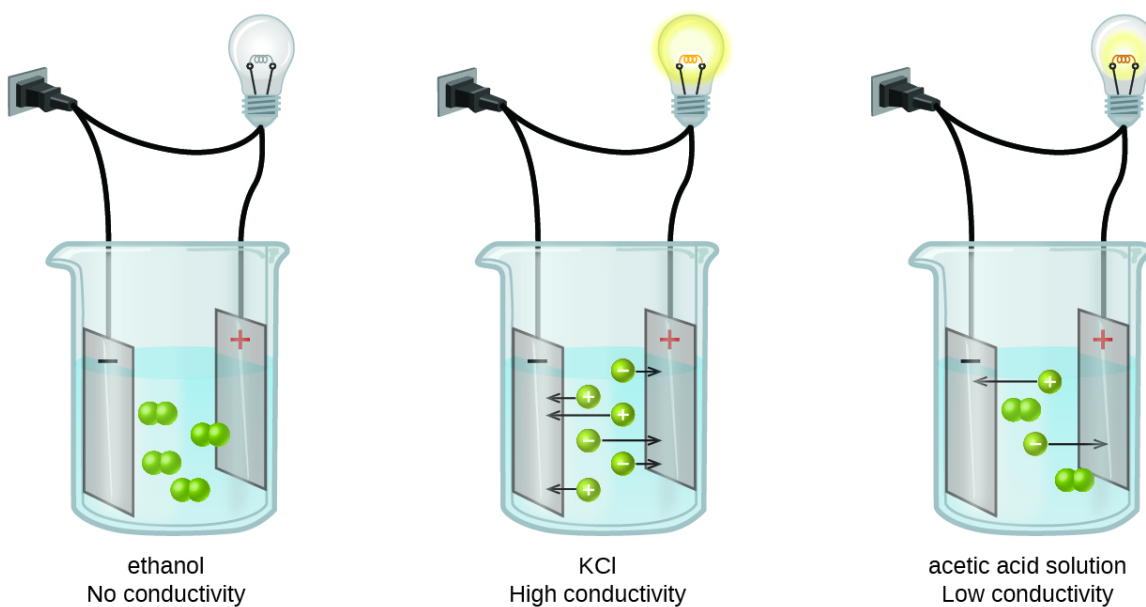
## Electrolytes

By the end of this module, you will be able to:

- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

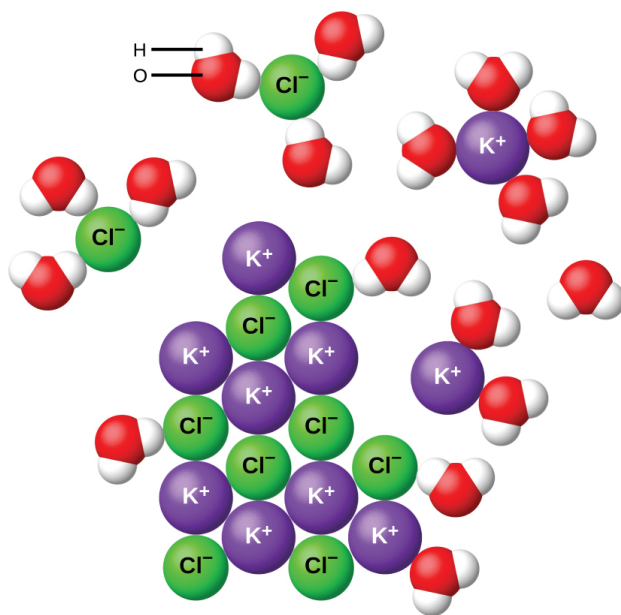
Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit ([\[link\]](#)).



Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

## Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in [\[link\]](#). The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction**. These attractions play an important role in the dissolution of ionic compounds in water.



As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the  $\text{K}^+$  and  $\text{Cl}^-$  ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as **dissociation**. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes. Even sparingly, soluble ionic compounds are strong electrolytes, since the small amount that does dissolve will dissociate completely.

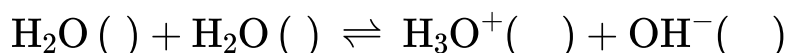
Consider what happens at the microscopic level when solid KCl is added to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and

they attract the negative (oxygen) ends to the positive potassium ions. The water molecules surround individual  $K^+$  and  $Cl^-$  ions, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as [\[link\]](#) shows. Overcoming the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution as the ions transition from fixed positions in the undissolved compound to widely dispersed, solvated ions in solution.

## Covalent Electrolytes

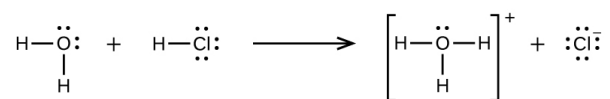
Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton ( $H^+$  ion) to another molecule of water, yielding hydronium and hydroxide ions.

**Equation:**



In some cases, solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, an aqueous solution of HCl is a very good conductor, indicating that an appreciable concentration of ions exists within the solution.

Because HCl is an *acid*, its molecules react with water, transferring  $H^+$  ions to form hydronium ions ( $H_3O^+$ ) and chloride ions ( $Cl^-$ ):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may



wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

## Key Concepts and Summary

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Explain why the ions  $\text{Na}^+$  and  $\text{Cl}^-$  are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules.

---

#### Solution:

Crystals of  $\text{NaCl}$  dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of the  $\text{NaCl}$  crystals.

### Exercise:

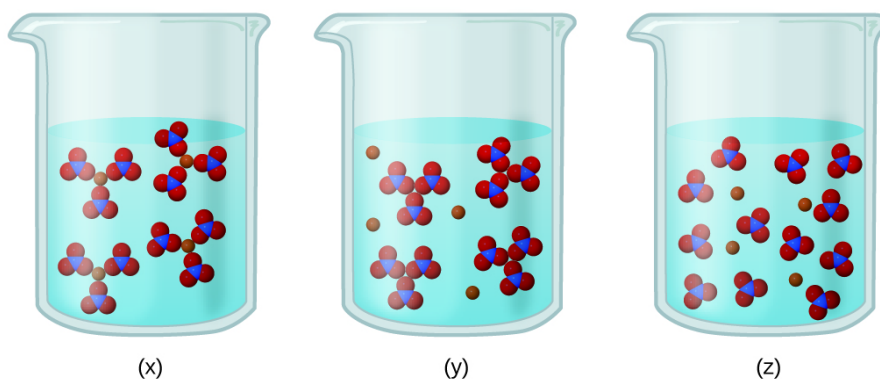
**Problem:**

Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.

**Exercise:**

**Problem:** Consider the solutions presented:

(a) Which of the following sketches best represents the ions in a solution of  $\text{Fe}(\text{NO}_3)_3(aq)$ ?



(b) Write a balanced chemical equation showing the products of the dissolution of  $\text{Fe}(\text{NO}_3)_3$ .

---

**Solution:**

(a)  $\text{Fe}(\text{NO}_3)_3$  is a strong electrolyte, thus it should completely dissociate into  $\text{Fe}^{3+}$  and  $\text{NO}_3^-$  ions. Therefore, (z) best represents the solution. (b)  $\text{Fe}(\text{NO}_3)_3(s) \longrightarrow \text{Fe}^{3+}(aq) + 3\text{NO}_3^-(aq)$

**Exercise:**

**Problem:**

Compare the processes that occur when methanol ( $\text{CH}_3\text{OH}$ ), hydrogen chloride ( $\text{HCl}$ ), and sodium hydroxide ( $\text{NaOH}$ ) dissolve in water.

Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

**Exercise:****Problem:**

What is the expected electrical conductivity of the following solutions?

(a)  $\text{NaOH}(aq)$

(b)  $\text{HCl}(aq)$

(c)  $\text{C}_6\text{H}_{12}\text{O}_6(aq)$  (glucose)

(d)  $\text{NH}_3(aq)$

---

**Solution:**

(a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)

**Exercise:****Problem:**

Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.

**Exercise:**

**Problem:**

Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:

- (a) the solutions in [\[link\]](#)
  - (b) methanol,  $\text{CH}_3\text{OH}$ , dissolved in ethanol,  $\text{C}_2\text{H}_5\text{OH}$
  - (c) methane,  $\text{CH}_4$ , dissolved in benzene,  $\text{C}_6\text{H}_6$
  - (d) the polar halocarbon  $\text{CF}_2\text{Cl}_2$  dissolved in the polar halocarbon  $\text{CF}_2\text{ClCFCl}_2$
  - (e)  $\text{O}_2(l)$  in  $\text{N}_2(l)$
- 

**Solution:**

(a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces

**Glossary**

dissociation

physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

electrolyte

substance that produces ions when dissolved in water

ion-dipole attraction

electrostatic attraction between an ion and a polar molecule

nonelectrolyte

substance that does not produce ions when dissolved in water

strong electrolyte

substance that dissociates or ionizes completely when dissolved in water

weak electrolyte

substance that ionizes only partially when dissolved in water

## Solubility

By the end of this module, you will be able to:

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of sugar to a glass of water, stirring until all the sugar has dissolved, and then adding a bit more. You can repeat this process until the sugar concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved sugar remains. The concentration of sugar in the solution at this point is known as its solubility.

The **solubility** of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*.

When a solute's concentration is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute's concentration is less than its solubility, the solution is said to be **unsaturated**. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

### Note:

Use this [interactive simulation](#) to prepare various saturated solutions.

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be **supersaturated**, and they are interesting examples of *nonequilibrium* states (a detailed treatment of this important concept is provided in the text chapters on equilibrium). For example, the carbonated beverage in an open container that has not yet “gone flat” is supersaturated with carbon dioxide gas; given time, the CO<sub>2</sub> concentration will decrease until it reaches its solubility.

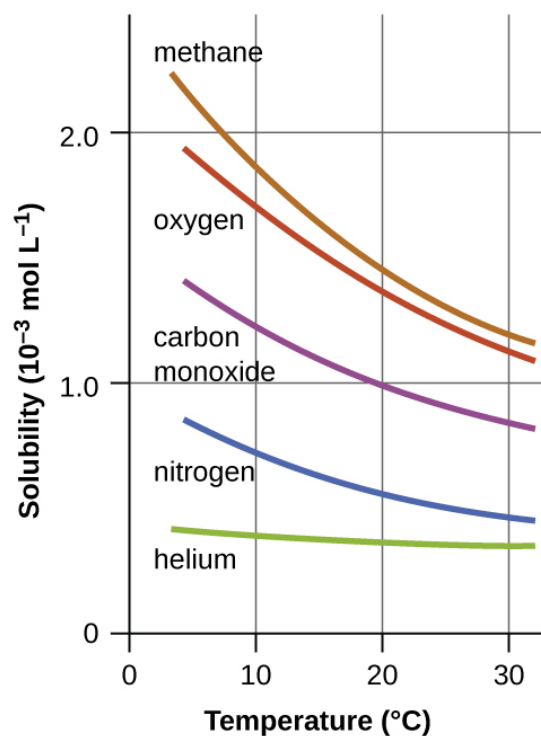
**Note:**

Watch this [impressive video](#) showing the precipitation of sodium acetate from a supersaturated solution.

## Solutions of Gases in Liquids

As for any solution, the solubility of a gas in a liquid is affected by the intermolecular attractive forces between solute and solvent species. Unlike solid and liquid solutes, however, there is no solute-solute intermolecular attraction to overcome when a gaseous solute dissolves in a liquid solvent (see [link](#)) since the atoms or molecules comprising a gas are far separated and experience negligible interactions. Consequently, solute-solvent interactions are the sole energetic factor affecting solubility. For example, the water solubility of oxygen is approximately three times greater than that of helium (there are greater dispersion forces between water and the larger oxygen molecules) but 100 times less than the solubility of chloromethane,  $\text{CHCl}_3$  (polar chloromethane molecules experience dipole–dipole attraction to polar water molecules). Likewise note the solubility of oxygen in hexane,  $\text{C}_6\text{H}_{14}$ , is approximately 20 times greater than it is in water because greater dispersion forces exist between oxygen and the larger hexane molecules.

Temperature is another factor affecting solubility, with gas solubility typically decreasing as temperature increases ([link](#)). This inverse relation between temperature and dissolved gas concentration is responsible for one of the major impacts of thermal pollution in natural waters.



The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills ([\[link\]](#)).





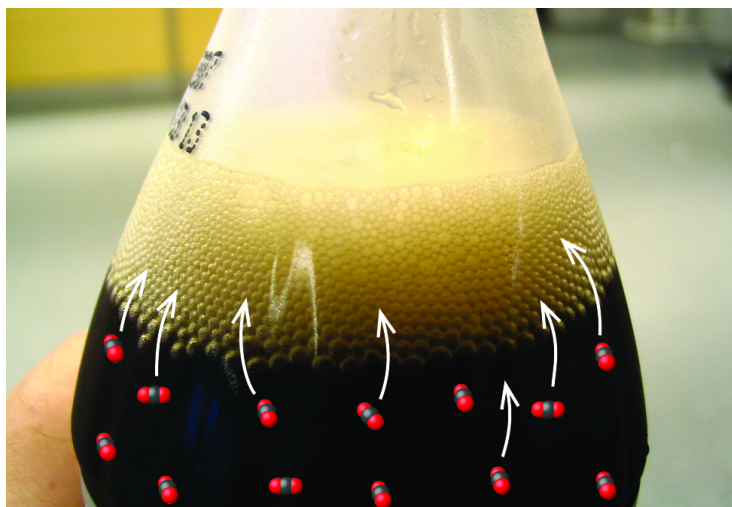
(a)



(b)

(a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with  $\text{CO}_2$  at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles ([link](#)). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”



Opening the bottle of carbonated beverage reduces the pressure of the *gaseous* carbon dioxide above the beverage. The solubility of CO<sub>2</sub> is thus lowered, and some *dissolved* carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility,  $C_g$ , and partial pressure,  $P_g$ , is a proportional one:

**Equation:**

$$C_g = kP_g$$

where  $k$  is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of **Henry's law**: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

**Example:**

**Application of Henry's Law**

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa is  $1.38 \times 10^{-3} \text{ mol L}^{-1}$ . Use Henry's

law to determine the solubility of oxygen when its partial pressure is 20.7 kPa, the approximate pressure of oxygen in earth's atmosphere.

**Solution**

According to Henry's law, for an ideal solution the solubility,  $C_g$ , of a gas ( $1.38 \times 10^{-3} \text{ mol L}^{-1}$ , in this case) is directly proportional to the pressure,  $P_g$ , of the undissolved gas above the solution (101.3 kPa in this case). Because both  $C_g$  and  $P_g$  are known, this relation can be rearranged and used to solve for  $k$ .

**Equation:**

$$\begin{aligned}C_g &= kP_g \\k &= \frac{C_g}{P_g} \\&= \frac{1.38 \times 10^{-3} \text{ mol L}^{-1}}{101.3 \text{ kPa}} \\&= 1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1}\end{aligned}$$

Now, use  $k$  to find the solubility at the lower pressure.

**Equation:**

$$\begin{aligned}C_g &= kP_g \\&= 1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \times 20.7 \text{ kPa} \\&= 2.82 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

**Check Your Learning**

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 152 torr resulted in the dissolution of  $1.45 \times 10^{-3} \text{ g}$  of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 760 torr.

**Note:**

**Answer:**

$7.25 \times 10^{-3}$  in 100.0 mL or 0.0725 g/L

**Example:****Thermal Pollution and Oxygen Solubility**

A certain species of freshwater trout requires a dissolved oxygen concentration of 7.5 mg/L. Could these fish thrive in a thermally polluted mountain stream (water temperature is 30.0 °C, partial pressure of atmospheric oxygen is 0.17 atm)?

**Solution**

First, compute the Henry's law constant for oxygen in water at the specified temperature of 30.0 °C (see [\[link\]](#)).

**Equation:**

$$k = \frac{C_g}{P_g} = 1.15 \times 10^{-3} \text{ mol/L/1.00 atm} = 1.15 \times 10^{-3} \text{ mol/L atm}$$

Then, use this  $k$  value to compute the oxygen solubility at the specified oxygen partial pressure, 0.17 atm.

**Equation:**

$$C_g = kP_g = (1.15 \times 10^{-3} \text{ mol/L atm}) (0.17 \text{ atm}) = 1.95 \times 10^{-4} \text{ mol/L}$$

Finally, convert this dissolved oxygen concentration from mol/L to mg/L.

**Equation:**

$$(1.95 \times 10^{-4} \text{ mol/L}) (32.0 \text{ g/1 mol}) (1000 \text{ mg/g}) = 6.2 \text{ mg/L.}$$

This concentration is lesser than the required minimum value of 7.5 mg/L, and so these trout would likely not thrive in the polluted stream.

**Check Your Learning**

What dissolved oxygen concentration is expected for the stream above when it returns to a normal summer time temperature of 15 °C?

**Note:****Answer:**

8.2 mg/L

**Note:****Decompression Sickness or “The Bends”**

Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth.

Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver’s blood are proportionally higher per Henry’s law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases become less soluble. If the ascent is too rapid, the gases escaping from the diver’s blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers ([\[link\]](#)).



(a)

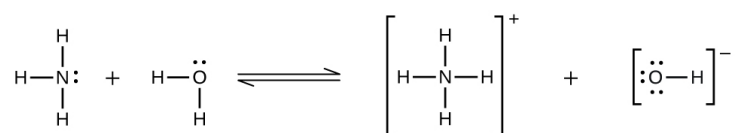


(b)

(a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Deviations from Henry’s law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water increases more rapidly with increasing pressure than predicted

by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos ([link](#)), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved  $\text{CO}_2$  were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a)



(b)

(a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A  $\text{CO}_2$  vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)



## Solutions of Liquids in Liquids

Some liquids may be mixed in any proportions to yield solutions; in other words, they have infinite mutual solubility and are said to be **miscible**. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in [\[link\]](#)) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline, mixtures of which are used as lubricating fuels for various types of outdoor power equipment (chainsaws, leaf blowers, and so on).



Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Miscible liquids are typically those with very similar polarities. Consider, for example, liquids that are polar or capable of hydrogen bonding. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called **immiscible**. Separate layers are formed when immiscible liquids are poured into the same container. Gasoline, oil ([link](#)), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. Relatively weak attractive forces between the polar water molecules and the nonpolar liquid molecules are not adequate to overcome much stronger hydrogen bonding between water molecules. The distinction between immiscibility and miscibility is really one of extent, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.





Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be **partially miscible**. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it.

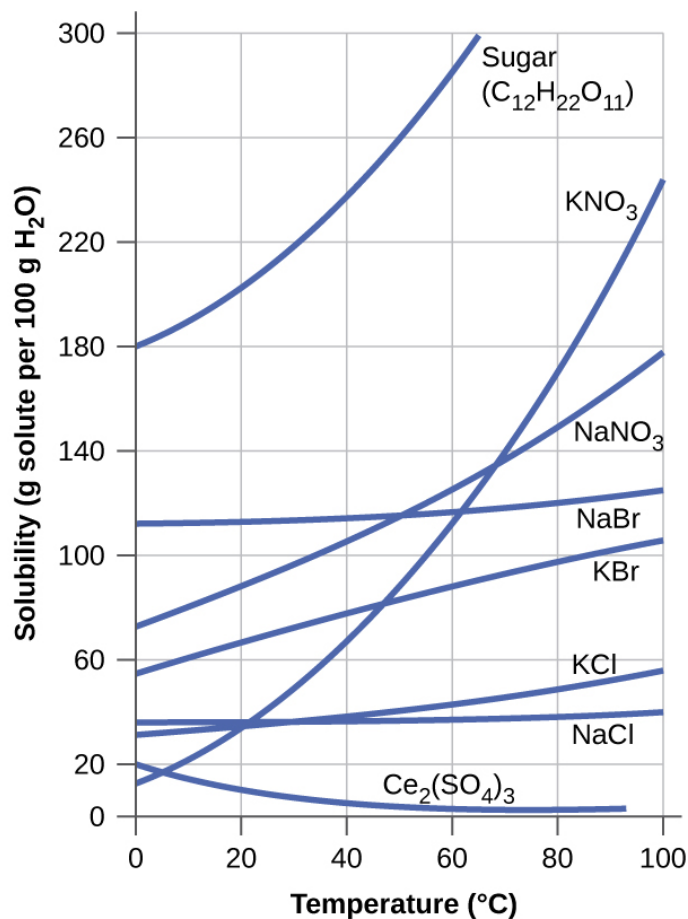
Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer ([link](#)).



Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine.  
(credit: Paul Flowers)

## Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of solids in water is shown by the solubility curves in [link](#). Reviewing these data indicates a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.



This graph shows how the solubility of several solids changes with temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in [\[link\]](#), take advantage of this behavior.



This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Veleta”/Wikimedia Commons)

**Note:**

This [video](#) shows the crystallization process occurring in a hand warmer.

## Key Concepts and Summary

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances’ atoms, ions, or molecules. This tendency to dissolve is quantified as a substance’s solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute’s concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry’s law.

## Key Equations

$$C_g = kP_g$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Suppose you are presented with a clear solution of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ . How could you determine whether the solution is unsaturated, saturated, or supersaturated?

### Exercise:

#### Problem:

Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.

---

#### Solution:

The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.

### Exercise:

#### Problem:

Suggest an explanation for the observations that ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is completely miscible with water and that ethanethiol,  $\text{C}_2\text{H}_5\text{SH}$ , is soluble only to the extent of 1.5 g per 100 mL of water.

### Exercise:

**Problem:**

Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C. See [\[link\]](#) for useful data, and report the computed percentage to one significant digit.

---

**Solution:**

40%

**Exercise:****Problem:**

Which of the following gases is expected to be most soluble in water? Explain your reasoning.

(a) CH<sub>4</sub>

(b) CCl<sub>4</sub>

(c) CHCl<sub>3</sub>

**Exercise:****Problem:**

At 0 °C and 1.00 atm, as much as 0.70 g of O<sub>2</sub> can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O<sub>2</sub> dissolve in 1 L of water?

---

**Solution:**

2.8 g

**Exercise:**

**Problem:** Refer to [\[link\]](#).

(a) How did the concentration of dissolved CO<sub>2</sub> in the beverage change when the bottle was opened?

(b) What caused this change?

(c) Is the beverage unsaturated, saturated, or supersaturated with CO<sub>2</sub>?

**Exercise:**

**Problem:**

The Henry's law constant for CO<sub>2</sub> is  $3.4 \times 10^{-2} \text{ M/atm}$  at 25 °C. Assuming ideal solution behavior, what pressure of carbon dioxide is needed to maintain a CO<sub>2</sub> concentration of 0.10 *M* in a can of lemon-lime soda?

---

**Solution:**

2.9 atm

**Exercise:**

**Problem:**

The Henry's law constant for O<sub>2</sub> is  $1.3 \times 10^{-3} \text{ M/atm}$  at 25 °C. Assuming ideal solution behavior, what mass of oxygen would be dissolved in a 40-L aquarium at 25 °C, assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O<sub>2</sub> is 0.21 atm?

**Exercise:**

**Problem:**

Assuming ideal solution behavior, how many liters of HCl gas, measured at 30.0 °C and 745 torr, are required to prepare 1.25 L of a 3.20-*M* solution of hydrochloric acid?

---

**Solution:**

102 L HCl

## Glossary

Henry's law

the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible

of negligible mutual solubility; typically refers to liquid substances

miscible

mutually soluble in all proportions; typically refers to liquid substances

partially miscible

of moderate mutual solubility; typically refers to liquid substances

saturated

of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility

extent to which a solute may be dissolved in water, or any solvent

supersaturated

of concentration that exceeds solubility; a nonequilibrium state

unsaturated

of concentration less than solubility



## Colligative Properties

By the end of this section, you will be able to:

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These **colligative properties** include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

## Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity ( $M$ ) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

**Equation:**

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction,  $X$ , of a component is the ratio of its molar amount to the total number of moles of all solution components:

**Equation:**

$$X_A = \frac{\text{mol A}}{\text{total mol of all components}}$$

By this definition, the sum of mole fractions for all solution components (the solvent and all solutes) is equal to one.

**Molality** is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

**Equation:**

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

**Example:**

**Calculating Mole Fraction and Molality**

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$ , in a solution prepared from  $2.22 \times 10^3 \text{ g}$  of ethylene glycol and  $2.00 \times 10^3 \text{ g}$  of water (approximately 2 L of glycol and 2 L of water)?

**Solution**

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the definition of mole fraction.

**Equation:**

$$\begin{aligned}\text{mol C}_2\text{H}_4(\text{OH})_2 &= 2.22 \times 10^3 \text{ g} \times \frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g C}_2\text{H}_4(\text{OH})_2} = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2 \\ \text{mol H}_2\text{O} &= 2.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 111 \text{ mol H}_2\text{O} \\ X_{\text{ethylene glycol}} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{(35.8 + 111) \text{ mol total}} = 0.244\end{aligned}$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) Derive moles of solute and mass of solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

**Equation:**

$$2.22 \times 10^3 \text{ g C}_2\text{H}_4(\text{OH})_2 \left( \frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g}} \right) = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2$$

Then, convert the mass of the water from grams to kilograms:

**Equation:**

$$2.00 \times 10^3 \text{ g H}_2\text{O} \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right) = 2.00 \text{ kg H}_2\text{O}$$

Finally, calculate molality per its definition:

**Equation:**

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

$$\text{molality} = \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{2 \text{ kg H}_2\text{O}}$$

$$\text{molality} = 17.9 \text{ } m$$

### Check Your Learning

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia,  $\text{NH}_3$ , dissolved in 125 g of water?

**Note:**

**Answer:**

$$7.14 \times 10^{-3}; 0.399 \text{ } m$$

### Example:

#### Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0  $m$  solution of sodium chloride.

#### Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

**Equation:**

$$\frac{3.0 \text{ mol NaCl}}{1 \text{ kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

**Equation:**

$$1.0 \text{ kg H}_2\text{O} \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) \left( \frac{\text{mol H}_2\text{O}}{18.02 \text{ g}} \right) = 55 \text{ mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

**Equation:**

$$\begin{aligned}
 X_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\
 X_{\text{H}_2\text{O}} &= \frac{55 \text{ mol H}_2\text{O}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\
 X_{\text{H}_2\text{O}} &= 0.95 \\
 X_{\text{NaCl}} &= \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\
 X_{\text{NaCl}} &= \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\
 X_{\text{NaCl}} &= 0.052
 \end{aligned}$$

### Check Your Learning

The mole fraction of iodine,  $\text{I}_2$ , dissolved in dichloromethane,  $\text{CH}_2\text{Cl}_2$ , is 0.115. What is the molal concentration,  $m$ , of iodine in this solution?

**Note:**

**Answer:**

1.50  $m$

### Example:

#### Molality and Molarity Conversions

Intravenous infusion of a 0.556  $M$  aqueous solution of glucose (density of 1.04 g/mL) is part of some post-operative recovery therapies. What is the molal concentration of glucose in this solution?

#### Solution

The provided molal concentration may be explicitly written as:

**Equation:**

$$M = 0.556 \text{ mol glucose/1 L solution}$$

Consider the definition of molality:

**Equation:**

$$m = \text{mol solute/kg solvent}$$

The amount of glucose in 1-L of this solution is 0.556 mol, so the mass of water in this volume of solution is needed.

First, compute the mass of 1.00 L of the solution:

**Equation:**

$$(1.0 \text{ L soln}) (1.04 \text{ g/mL}) (1000 \text{ mL/1L}) (1 \text{ kg/1000 g}) = 1.04 \text{ kg soln}$$

This is the mass of both the water and its solute, glucose, and so the mass of glucose must be subtracted. Compute the mass of glucose from its molar amount:

**Equation:**

$$(0.556 \text{ mol glucose}) (180.2 \text{ g/1 mol}) = 100.2 \text{ g or } 0.1002 \text{ kg}$$

Subtracting the mass of glucose yields the mass of water in the solution:

**Equation:**

$$1.02 \text{ kg solution} - 0.1002 \text{ kg glucose} = 0.92 \text{ kg water}$$

Finally, the molality of glucose in this solution is computed as:

**Equation:**

$$m = 0.556 \text{ mol glucose} / 0.92 \text{ kg water} = 0.60 \text{ m}$$

### Check Your Learning

Nitric acid,  $\text{HNO}_3(aq)$ , is commercially available as a 33.7 m aqueous solution (density = 1.35 g/mL). What is the molarity of this solution?

**Note:**

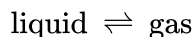
**Answer:**

14.6 M

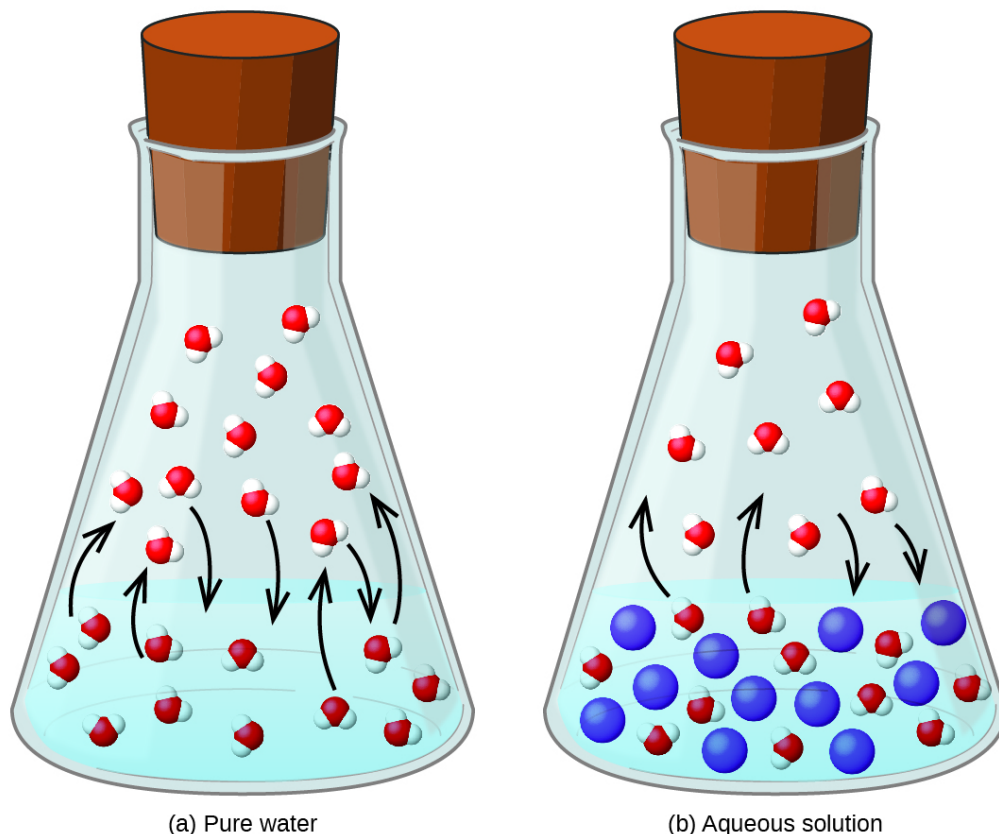
## Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

**Equation:**



Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) ([Link](#)). While this interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the more dispersed nature of matter in a solution, compared to separate solvent and solute phases, serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.



The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by **Raoult's law**: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

**Equation:**

$$P_A = X_A P_A^*$$

where  $P_A$  is the partial pressure exerted by component A in the solution,  $P_A^*$  is the vapor pressure of pure A, and  $X_A$  is the mole fraction of A in the solution.

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapor pressure exerted by a solution containing  $i$  components is

**Equation:**

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^*$$

A nonvolatile substance is one whose vapor pressure is negligible ( $P^* \approx 0$ ), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

**Equation:**

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^*$$

**Example:**

### Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin,  $\text{C}_3\text{H}_5(\text{OH})_3$ , and 184.4 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

**Solution**

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult's law as:

**Equation:**

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^*$$

First, calculate the molar amounts of each solution component using the provided mass data.

**Equation:**

$$\begin{aligned} 92.1 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3 &\times \frac{1 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3}{92.094 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3} = 1.00 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3 \\ 184.4 \text{ g } \text{C}_2\text{H}_5\text{OH} &\times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.069 \text{ g } \text{C}_2\text{H}_5\text{OH}} = 4.000 \text{ mol } \text{C}_2\text{H}_5\text{OH} \end{aligned}$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapor pressure.

**Equation:**

$$\begin{aligned} X_{\text{C}_2\text{H}_5\text{OH}} &= \frac{4.000 \text{ mol}}{(1.00 \text{ mol} + 4.000 \text{ mol})} = 0.800 \\ P_{\text{solv}} &= X_{\text{solv}} P_{\text{solv}}^* = 0.800 \times 0.178 \text{ atm} = 0.142 \text{ atm} \end{aligned}$$

### Check Your Learning

A solution contains 5.00 g of urea,  $\text{CO}(\text{NH}_2)_2$  (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution assuming ideal behavior?

**Note:**

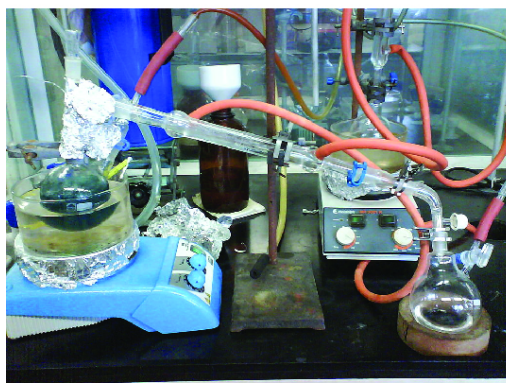
**Answer:**

23.4 torr

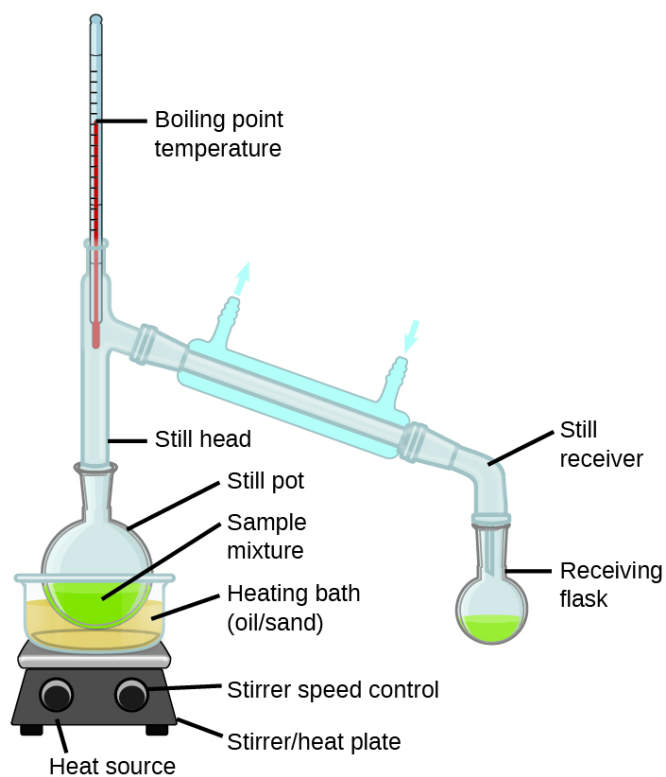
## Distillation of Solutions

Solutions whose components have significantly different vapor pressures may be separated by a selective vaporization process known as distillation. Consider the simple case of a mixture of two volatile liquids, A and B, with A being the more volatile liquid. Raoult's law can be used to show that the vapor above the solution is enriched in component A, that is, the mole fraction of A in the vapor is greater than the mole fraction of A in the liquid (see end-of-chapter Exercise 65). By appropriately heating the mixture, component A may be vaporized, condensed, and collected—effectively separating it from component B.

Distillation is widely applied in both laboratory and industrial settings, being used to refine petroleum, to isolate fermentation products, and to purify water. A typical apparatus for laboratory-scale distillations is shown in [\[link\]](#).



(a)

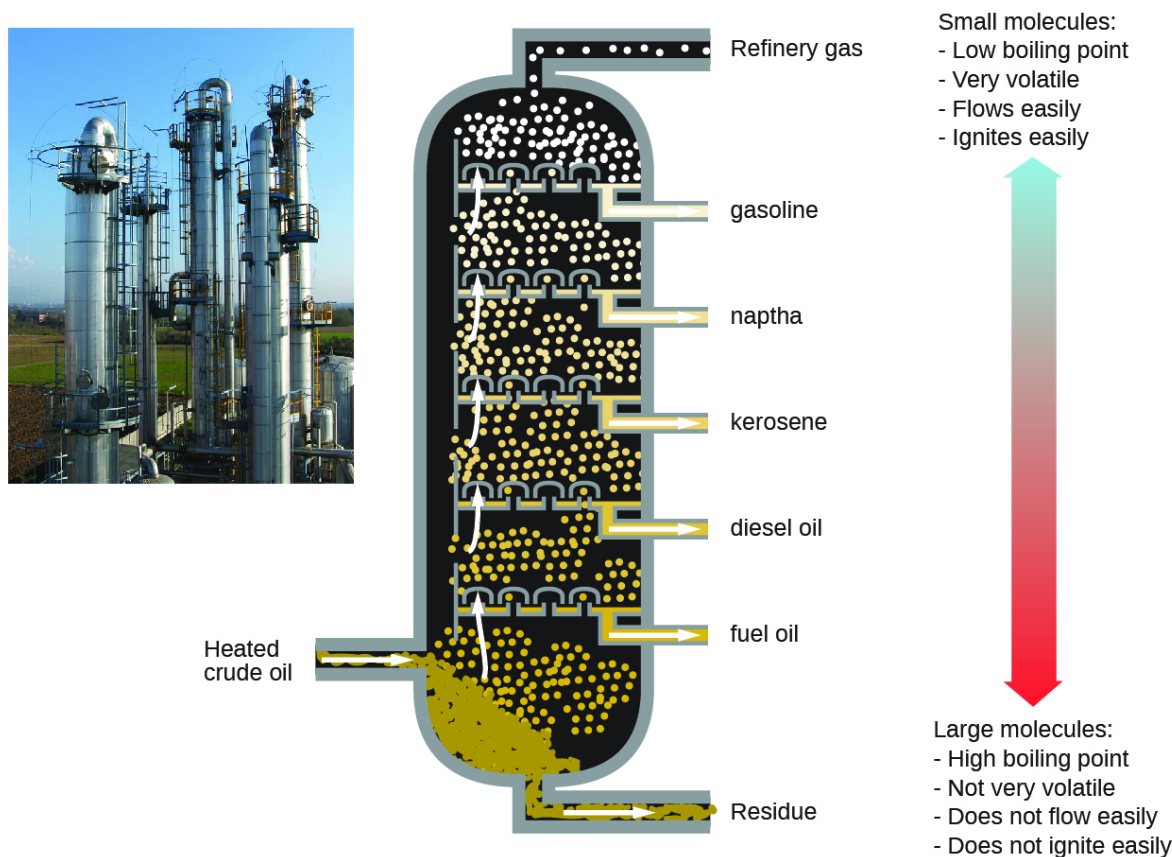


(b)

A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons)



Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in [\[link\]](#).



Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

## Boiling Point Elevation

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Vapor pressure increases with temperature, and so a solution will require a higher temperature than will pure solvent to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent,  $\Delta T_b$ , is called **boiling point elevation** and is directly proportional to the molal concentration of solute species:

**Equation:**

$$\Delta T_b = K_b m$$

where  $K_b$  is the **boiling point elevation constant**, or the *ebullioscopic constant* and  $m$  is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of  $K_b$  for several solvents are listed in [\[link\]](#).

Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents				
Solvent	Boiling Point (°C at 1 atm)	$K_b$ (°C $m^{-1}$ )	Freezing Point (°C at 1 atm)	$K_f$ (°C $m^{-1}$ )
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

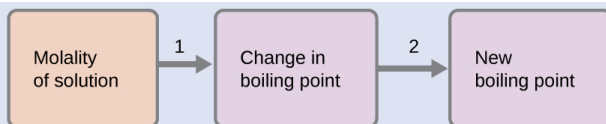
The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1  $m$  aqueous solution of sucrose (342 g/mol) and a 1  $m$  aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

**Example:****Calculating the Boiling Point of a Solution**

Assuming ideal solution behavior, what is the boiling point of a 0.33  $m$  solution of a nonvolatile solute in benzene?

**Solution**

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



Calculate the change in boiling point. **Equation:**

$$\Delta T_b = K_b m = 2.53\text{ }^{\circ}\text{C } m^{-1} \times 0.33\text{ } m = 0.83\text{ }^{\circ}\text{C}$$

Add the boiling point elevation to the pure solvent's boiling point. **Equation:**

$$\text{Boiling temperature} = 80.1\text{ }^{\circ}\text{C} + 0.83\text{ }^{\circ}\text{C} = 80.9\text{ }^{\circ}\text{C}$$

### Check Your Learning

Assuming ideal solution behavior, what is the boiling point of the antifreeze described in [\[link\]](#)?

**Note:**

**Answer:**

109.2 °C

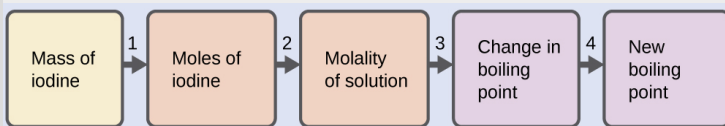
### Example:

#### The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine,  $\text{I}_2$ , in 800.0 g of chloroform,  $\text{CHCl}_3$ , assuming that the iodine is nonvolatile and that the solution is ideal.

#### Solution

A four-step approach to solving this problem is outlined below.



Convert from grams to moles of  $\text{I}_2$  using the molar mass of  $\text{I}_2$  in the unit conversion factor. Result: 0.363 mol

Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms. Result: 0.454 m

Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes. Result: 1.65 °C

Determine the new boiling point from the boiling point of the pure solvent and the change. Result: 62.91 °C Check each result as a self-assessment.

### Check Your Learning

What is the boiling point of a solution of 1.0 g of glycerin,  $\text{C}_3\text{H}_5(\text{OH})_3$ , in 47.8 g of water? Assume an ideal solution.

**Note:**

**Answer:**

100.12 °C

## Freezing Point Depression

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt ([link](#)), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Rock salt (NaCl), calcium chloride (CaCl<sub>2</sub>), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent,  $\Delta T_f$ , is called the **freezing point depression** and is directly proportional to the molal concentration of the solute

**Equation:**

$$\Delta T_f = K_f m$$

where  $m$  is the molal concentration of the solute and  $K_f$  is called the **freezing point depression constant** (or *cryoscopic constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of  $K_f$  for several solvents are listed in [link](#).

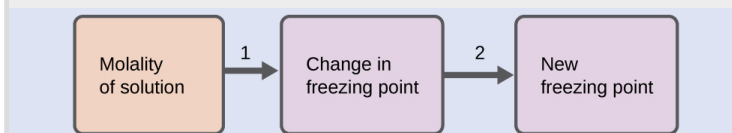
**Example:**

**Calculation of the Freezing Point of a Solution**

Assuming ideal solution behavior, what is the freezing point of the 0.33 *m* solution of a nonvolatile nonelectrolyte solute in benzene described in [\[link\]](#)?

**Solution**

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



Calculate the change in freezing point. **Equation:**

$$\Delta T_f = K_f m = 5.12\text{ }^{\circ}\text{C } m^{-1} \times 0.33\text{ } m = 1.7\text{ }^{\circ}\text{C}$$

Subtract the freezing point change observed from the pure solvent's freezing point. **Equation:**

$$\text{Freezing Temperature} = 5.5\text{ }^{\circ}\text{C} - 1.7\text{ }^{\circ}\text{C} = 3.8\text{ }^{\circ}\text{C}$$

**Check Your Learning**

Assuming ideal solution behavior, what is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

**Note:**

**Answer:**

−9.3 °C

**Note:**

**Colligative Properties and De-Icing**

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride (“rock salt”) for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already

formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft ([link](#)).



(a)

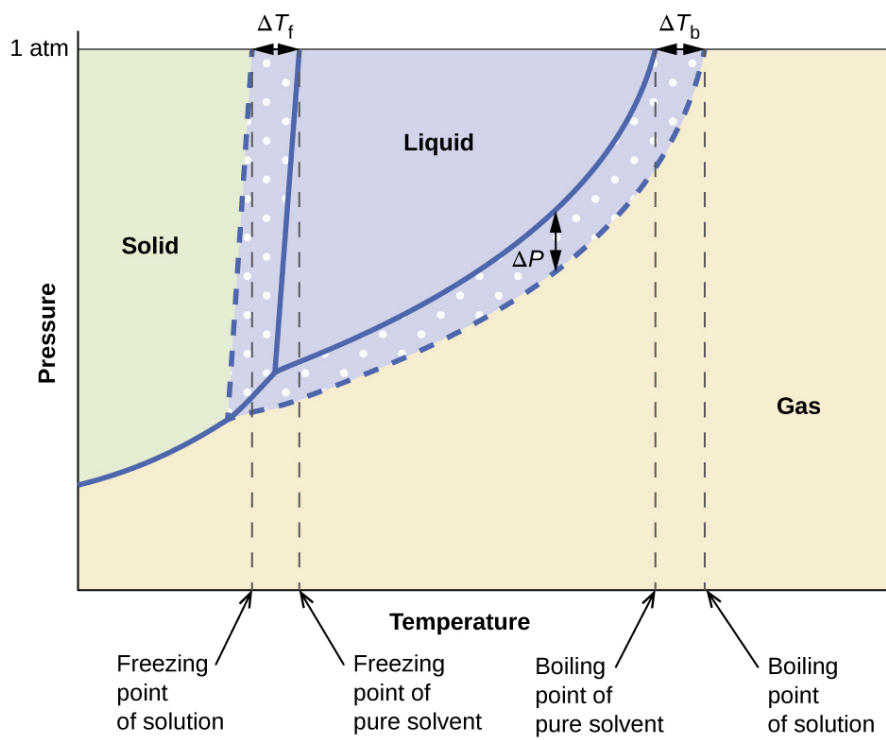


(b)

Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

## Phase Diagram for a Solution

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid ([link](#)).



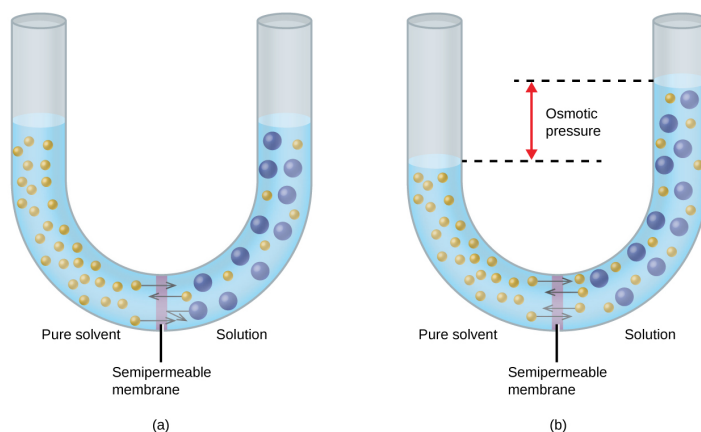
Phase diagrams for a pure solvent (solid curves) and a solution formed by dissolving nonvolatile solute in the solvent (dashed curves).

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*,  $\Delta P$ , that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation,  $\Delta T_b$ , associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression,  $\Delta T_f$ , that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed of solvent only, and so transitions between these phases are not subject to colligative effects.

## Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as **semipermeable membranes**.

Consider the apparatus illustrated in [\[link\]](#), in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as **osmosis**.



(a) A solution and pure solvent are initially separated

by an osmotic membrane. (b) Net transfer of solvent molecules to the solution occurs until its osmotic pressure yields equal rates of transfer in both directions.

When osmosis is carried out in an apparatus like that shown in [\[link\]](#), the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the **osmotic pressure ( $\Pi$ )** of the solution. The osmotic pressure of a dilute solution is related to its solute molarity,  $M$ , and absolute temperature,  $T$ , according to the equation

**Equation:**

$$\Pi = MRT$$

where  $R$  is the universal gas constant.

**Example:**

**Calculation of Osmotic Pressure**

Assuming ideal solution behavior, what is the osmotic pressure (atm) of a 0.30  $M$  solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

**Solution**

Find the osmotic pressure,  $\Pi$ , using the formula  $\Pi = MRT$ , where  $T$  is on the Kelvin scale (310 K) and the value of  $R$  is expressed in appropriate units (0.08206 L atm/mol K).

**Equation:**

$$\begin{aligned}\Pi &= MRT \\ &= 0.30 \text{ mol/L} \times 0.08206 \text{ L atm/mol K} \times 310 \text{ K} \\ &= 7.6 \text{ atm}\end{aligned}$$

**Check Your Learning**

Assuming ideal solution behavior, what is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol,  $\text{CH}_3\text{OH}$ , in water at 37 °C?

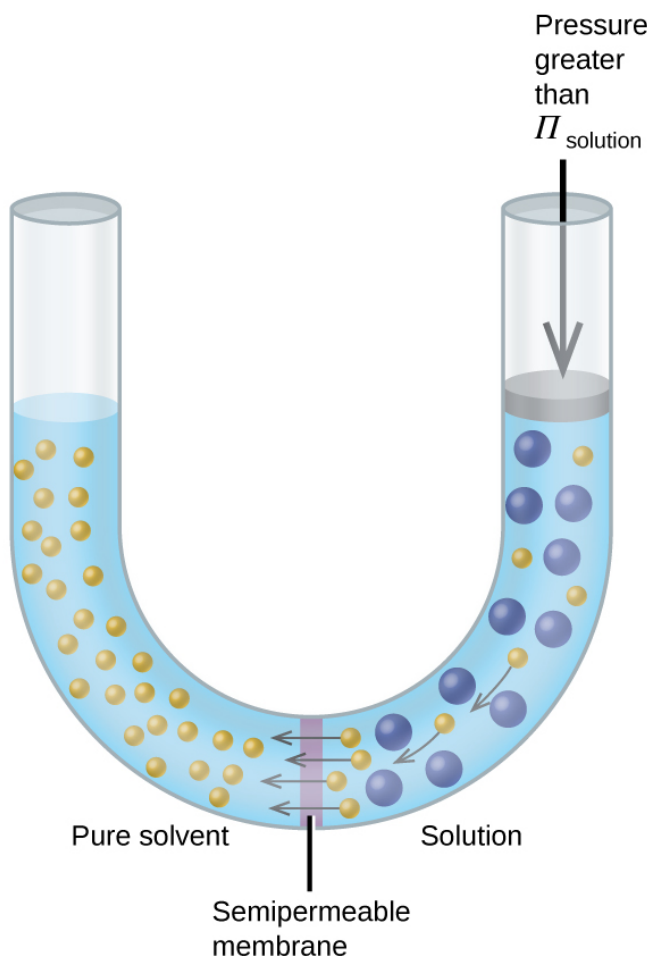
**Note:**

**Answer:**

5.3 atm



If a solution is placed in an apparatus like the one shown in [\[link\]](#), applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.



Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

**Note:****Reverse Osmosis Water Purification**

In the process of osmosis, diffusion serves to move water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. Osmotic pressure is the amount of pressure that must be applied to the more concentrated solution to cause osmosis to stop. If greater pressure is applied, the water will go from the more concentrated solution to a less concentrated (more pure) solution. This is called reverse osmosis. Reverse osmosis (RO) is used to purify water in many applications, from desalination plants in coastal cities, to water-purifying machines in grocery stores ([\[link\]](#)), and smaller reverse-osmosis household units. With a hand-operated pump, small RO

units can be used in third-world countries, disaster areas, and in lifeboats. Our military forces have a variety of generator-operated RO units that can be transported in vehicles to remote locations.



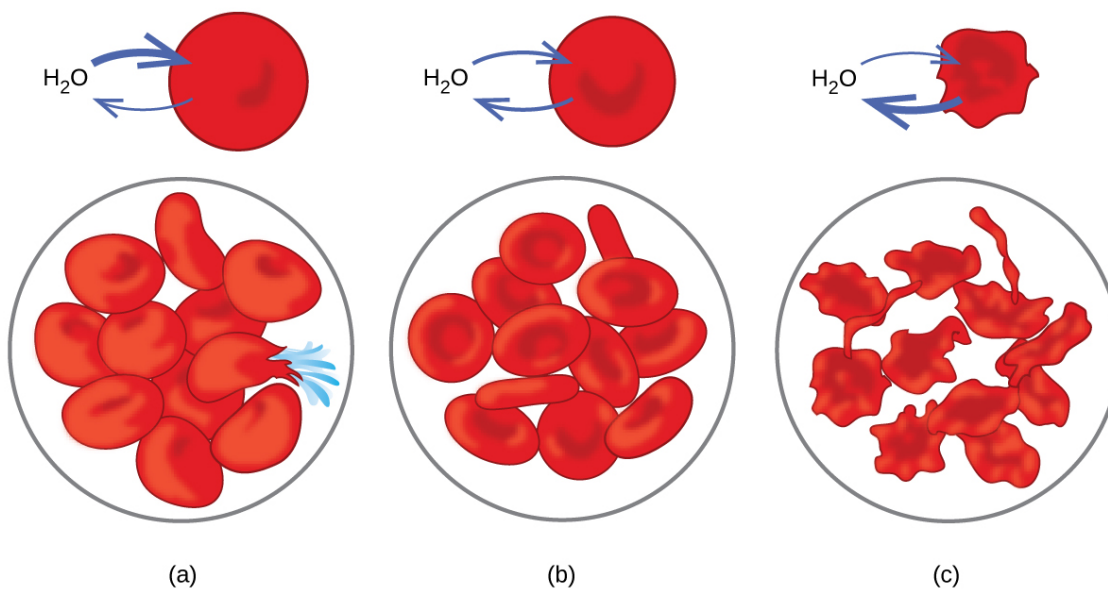
(a)



(b)

Reverse osmosis systems for purifying drinking water are shown here on (a) small and (b) large scales. (credit a: modification of work by Jerry Kirkhart; credit b: modification of work by Willard J. Lathrop)

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solute concentrations in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be **isotonic** with blood serum. If a less concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called **hemolysis**. When a more concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called **crenation**. These effects are illustrated in [\[link\]](#).



Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons)

## Determination of Molar Masses

Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the number of solute species present in a given amount of solution. Consequently, measuring one of these properties for a solution prepared using a known mass of solute permits determination of the solute’s molar mass.

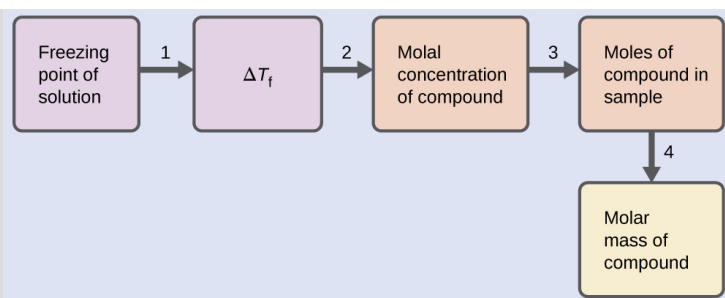
### Example:

#### Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

#### Solution

Solve this problem using the following steps.



Determine the change in freezing point from the [\(link\)](#). **Equation:**  
 observed freezing point and the freezing point of pure benzene

$$\Delta T_f = 5.5^\circ\text{C} - 2.32^\circ\text{C} = 3.2^\circ\text{C}$$

Determine the molal concentration from  $K_f$ , the freezing point depression constant for benzene [\(link\)](#), and  $\Delta T_f$ . **Equation:**

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2^\circ\text{C}}{5.12^\circ\text{C } m^{-1}} = 0.63 m$$

Determine the number **Equation:**

of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.

$$\text{Moles of solute} = \frac{0.63 \text{ mol solute}}{1.00 \text{ kg solvent}} \times 0.0550 \text{ kg solvent} = 0.035 \text{ mol}$$

Determine the molar mass from the mass of the solute and the number of moles in that mass. **Equation:**

$$\text{Molar mass} = \frac{4.00 \text{ g}}{0.035 \text{ mol}} = 1.1 \times 10^2 \text{ g/mol}$$

### Check Your Learning

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of  $64.5^\circ\text{C}$ . Assuming ideal solution behavior, what is the molar mass of this compound?

**Note:**

**Answer:**

$$1.8 \times 10^2 \text{ g/mol}$$

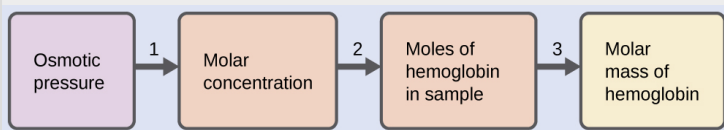
### Example:

#### Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at  $22^\circ\text{C}$ . Assuming ideal solution behavior, what is the molar mass of hemoglobin?

### Solution

Here is one set of steps that can be used to solve the problem:



Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.

Equation:

$$\Pi = \frac{5.9 \text{ torr} \times 1 \text{ atm}}{760 \text{ torr}} = 7.8 \times 10^{-3} \text{ atm}$$
$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm/mol K})(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$$

Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.

Equation:

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L solution}} \times 0.500 \text{ L solution} = 1.6 \times 10^{-4} \text{ mol}$$

Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.

Equation:

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^4 \text{ g/mol}$$

### Check Your Learning

Assuming ideal solution behavior, what is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

**Note:**

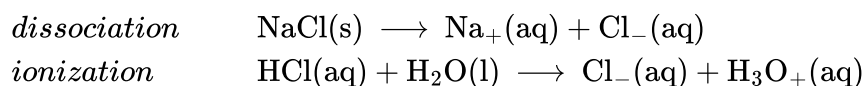
**Answer:**

$$3 \times 10^4 \text{ g/mol}$$

## Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the identity, of solute species dissolved. The concentration terms in the equations for various colligative properties (freezing point depression, boiling point elevation, osmotic pressure) pertain to *all solute species present in the solution*. For the solutions considered thus far in this chapter, the solutes have been nonelectrolytes that dissolve physically without dissociation or any other accompanying process. Each molecule that dissolves yields one dissolved solute molecule. The dissolution of an electrolyte, however, is not this simple, as illustrated by the two common examples below:

**Equation:**



Considering the first of these examples, and assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na<sup>+</sup> and 1.0 mol Cl<sup>−</sup>) per each kilogram of water, and its freezing point depression is expected to be

**Equation:**

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86^\circ\text{C kg water/mol ion} = 3.7^\circ\text{C}.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The **van't Hoff factor (*i*)** is defined as the ratio of solute particles in solution to the number of formula units dissolved:

**Equation:**

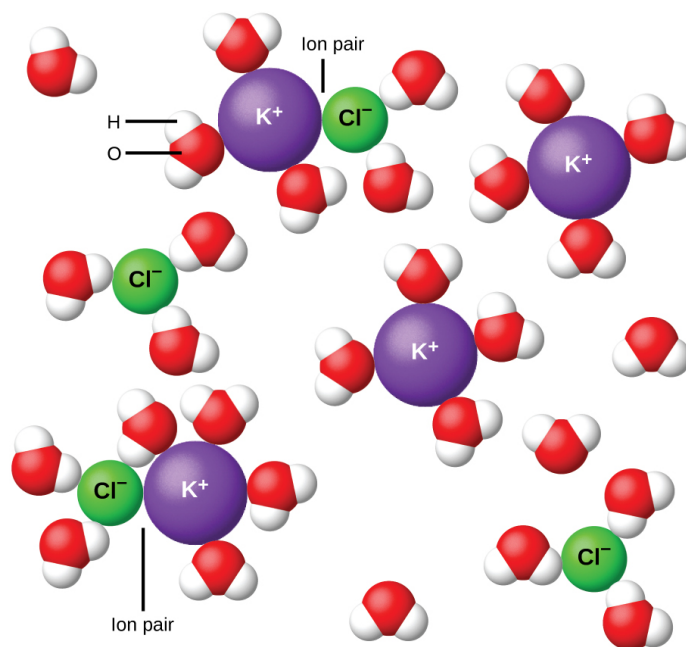
$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in [\[link\]](#).

Predicated and Measured van't Hoff Factors for Several 0.050 <i>m</i> Aqueous Solutions				
Formula unit	Classification	Dissolution products	<i>i</i> (predicted)	<i>i</i> (measured)

Predicated and Measured van't Hoff Factors for Several 0.050 <i>m</i> Aqueous Solutions				
Formula unit	Classification	Dissolution products	<i>i</i> (predicted)	<i>i</i> (measured)
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (glucose)	Nonelectrolyte	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	1	1.0
NaCl	Strong electrolyte	Na <sup>+</sup> , Cl <sup>-</sup>	2	1.9
HCl	Strong electrolyte (acid)	H <sub>3</sub> O <sup>+</sup> , Cl <sup>-</sup>	2	1.9
MgSO <sub>4</sub>	Strong electrolyte	Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> ,	2	1.3
MgCl <sub>2</sub>	Strong electrolyte	Mg <sup>2+</sup> , 2Cl <sup>-</sup>	3	2.7
FeCl <sub>3</sub>	Strong electrolyte	Fe <sup>3+</sup> , 3Cl <sup>-</sup>	4	3.4

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles ([\[link\]](#)). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the **activity**, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in [\[link\]](#) are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.



Dissociation of ionic compounds in water is not always complete due to the formation of ion pairs.

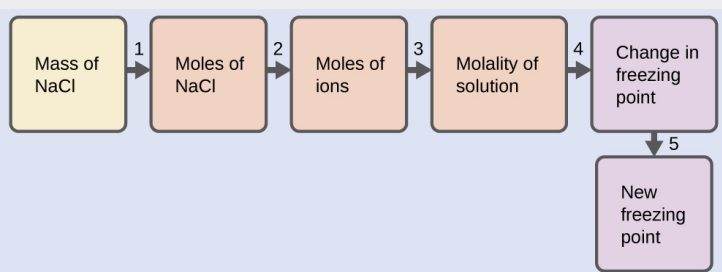
### Example:

#### The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Use this information and a predicted value for the van't Hoff factor ([\[link\]](#)) to determine the freezing temperature the solution (assume ideal solution behavior).

#### Solution

Solve this problem using the following series of steps.



Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor. Result: 0.072 mol NaCl

Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl). Result: 0.14 mol ions

Determine the molality of the ions in the solution from the number of moles of ions and the Result: m



mass of solvent, in kilograms. 1.2  
 Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes. Result: 2.1 °C  
 Determine the new freezing point from the freezing point of the pure solvent and the change. Result: -2.1 °C  
 Check each result as a self-assessment, taking care to avoid rounding errors by retaining guard digits in each step's result for computing the next step's result.

### Check Your Learning

Assuming complete dissociation and ideal solution behavior, calculate the freezing point of a solution of 0.724 g of CaCl<sub>2</sub> in 175 g of water.

**Note:**

**Answer:**

-0.208 °C

## Key Concepts and Summary

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

## Key Equations

$$(P_A = X_A P_A^*)$$

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^*$$

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^*$$

$$\Delta T_b = K_b m$$

$$\Delta T_f = K_f m$$

$$\Pi = MRT$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?

### Exercise:

#### Problem:

What is the microscopic explanation for the macroscopic behavior illustrated in [\[link\]](#)?

#### Solution:

The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.

### Exercise:

#### Problem:

Sketch a qualitative graph of the pressure versus time for water vapor above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.

### Exercise:

#### Problem:

A solution of potassium nitrate, an electrolyte, and a solution of glycerin ( $\text{C}_3\text{H}_5(\text{OH})_3$ ), a nonelectrolyte, both boil at  $100.3^\circ\text{C}$ . What other physical properties of the two solutions are identical?

#### Solution:

Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapor pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.

### Exercise:

#### Problem:

What are the mole fractions of  $\text{H}_3\text{PO}_4$  and water in a solution of 14.5 g of  $\text{H}_3\text{PO}_4$  in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

**Exercise:**

**Problem:**

What are the mole fractions of  $\text{HNO}_3$  and water in a concentrated solution of nitric acid (68.0%  $\text{HNO}_3$  by mass)?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

---

**Solution:**

(a) Find number of moles of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  in 100 g of the solution. Find the mole fractions for the components. (b) The mole fraction of  $\text{HNO}_3$  is 0.378. The mole fraction of  $\text{H}_2\text{O}$  is 0.622.

**Exercise:**

**Problem:** Calculate the mole fraction of each solute and solvent:

(a) 583 g of  $\text{H}_2\text{SO}_4$  in 1.50 kg of water—the acid solution used in an automobile battery

(b) 0.86 g of  $\text{NaCl}$  in  $1.00 \times 10^2$  g of water—a solution of sodium chloride for intravenous injection

(c) 46.85 g of codeine,  $\text{C}_{18}\text{H}_{21}\text{NO}_3$ , in 125.5 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$

(d) 25 g of  $\text{I}_2$  in 125 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$

**Exercise:**

**Problem:** Calculate the mole fraction of each solute and solvent:

(a) 0.710 kg of sodium carbonate (washing soda),  $\text{Na}_2\text{CO}_3$ , in 10.0 kg of water—a saturated solution at  $0^\circ\text{C}$

(b) 125 g of  $\text{NH}_4\text{NO}_3$  in 275 g of water—a mixture used to make an instant ice pack

(c) 25 g of  $\text{Cl}_2$  in 125 g of dichloromethane,  $\text{CH}_2\text{Cl}_2$

(d) 0.372 g of tetrahydropyridine,  $\text{C}_5\text{H}_9\text{N}$ , in 125 g of chloroform,  $\text{CHCl}_3$

---

**Solution:**

(a)  $X_{\text{Na}_2\text{CO}_3} = 0.0119$ ;  $X_{\text{H}_2\text{O}} = 0.988$ ; (b)  $X_{\text{NH}_4\text{NO}_3} = 0.0928$ ;  $X_{\text{H}_2\text{O}} = 0.907$ ; (c)  $X_{\text{Cl}_2} = 0.192$ ;  $X_{\text{CH}_2\text{Cl}_2} = 0.808$ ; (d)  $X_{\text{C}_5\text{H}_9\text{N}} = 0.00426$ ;  $X_{\text{CHCl}_3} = 0.997$

**Exercise:**

**Problem:**

Calculate the mole fractions of methanol,  $\text{CH}_3\text{OH}$ ; ethanol,  $\text{C}_2\text{H}_5\text{OH}$ ; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)

**Exercise:**

**Problem:** What is the difference between a 1  $M$  solution and a 1  $m$  solution?

---

**Solution:**

In a 1  $M$  solution, the mole is contained in exactly 1 L of solution. In a 1  $m$  solution, the mole is contained in exactly 1 kg of solvent.

**Exercise:****Problem:**

What is the molality of phosphoric acid,  $\text{H}_3\text{PO}_4$ , in a solution of 14.5 g of  $\text{H}_3\text{PO}_4$  in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

**Exercise:****Problem:**

What is the molality of nitric acid in a concentrated solution of nitric acid (68.0%  $\text{HNO}_3$  by mass)?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

---

**Solution:**

(a) Determine the molar mass of  $\text{HNO}_3$ . Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality. (b) 33.7  $m$

**Exercise:**

**Problem:** Calculate the molality of each of the following solutions:

(a) 583 g of  $\text{H}_2\text{SO}_4$  in 1.50 kg of water—the acid solution used in an automobile battery

(b) 0.86 g of  $\text{NaCl}$  in  $1.00 \times 10^2$  g of water—a solution of sodium chloride for intravenous injection

(c) 46.85 g of codeine,  $\text{C}_{18}\text{H}_{21}\text{NO}_3$ , in 125.5 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$

(d) 25 g of  $\text{I}_2$  in 125 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$

**Exercise:**

**Problem:** Calculate the molality of each of the following solutions:

- (a) 0.710 kg of sodium carbonate (washing soda),  $\text{Na}_2\text{CO}_3$ , in 10.0 kg of water—a saturated solution at  $0^\circ\text{C}$
  - (b) 125 g of  $\text{NH}_4\text{NO}_3$  in 275 g of water—a mixture used to make an instant ice pack
  - (c) 25 g of  $\text{Cl}_2$  in 125 g of dichloromethane,  $\text{CH}_2\text{Cl}_2$
  - (d) 0.372 g of tetrahydropyridine,  $\text{C}_5\text{H}_9\text{N}$ , in 125 g of chloroform,  $\text{CHCl}_3$
- 

**Solution:**

- (a)  $6.70 \times 10^{-1} m$ ; (b)  $5.67 m$ ; (c)  $2.8 m$ ; (d)  $0.0358 m$

**Exercise:**

**Problem:**

The concentration of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , in normal spinal fluid is  $\frac{75 \text{ mg}}{100 \text{ g}}$ . What is the molality of the solution?

**Exercise:**

**Problem:**

A 13.0% solution of  $\text{K}_2\text{CO}_3$  by mass has a density of  $1.09 \text{ g/cm}^3$ . Calculate the molality of the solution.

---

**Solution:**

$1.08 m$

**Exercise:**

**Problem:**

Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?

**Exercise:**

**Problem:**

Assuming ideal solution behavior, what is the boiling point of a solution of 115.0 g of nonvolatile sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , in 350.0 g of water?

- (a) Outline the steps necessary to answer the question
  - (b) Answer the question
- 

**Solution:**

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point. (b) 100.5 °C

**Exercise:**

**Problem:**

Assuming ideal solution behavior, what is the boiling point of a solution of 9.04 g of I<sub>2</sub> in 75.5 g of benzene, assuming the I<sub>2</sub> is nonvolatile?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

**Exercise:**

**Problem:**

Assuming ideal solution behavior, what is the freezing temperature of a solution of 115.0 g of sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, in 350.0 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

---

**Solution:**

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new freezing temperature. (b) -1.8 °C

**Exercise:**

**Problem:**

Assuming ideal solution behavior, what is the freezing point of a solution of 9.04 g of I<sub>2</sub> in 75.5 g of benzene?

(a) Outline the steps necessary to answer the following question.

(b) Answer the question.

**Exercise:**

**Problem:**

Assuming ideal solution behavior, what is the osmotic pressure of an aqueous solution of 1.64 g of Ca(NO<sub>3</sub>)<sub>2</sub> in water at 25 °C? The volume of the solution is 275 mL.

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

---

**Solution:**

(a) Determine the molar mass of  $\text{Ca}(\text{NO}_3)_2$ ; determine the number of moles of  $\text{Ca}(\text{NO}_3)_2$  in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure. (b) 2.67 atm

**Exercise:****Problem:**

Assuming ideal solution behavior, what is osmotic pressure of a solution of bovine insulin (molar mass,  $5700 \text{ g mol}^{-1}$ ) at  $18^\circ\text{C}$  if 100.0 mL of the solution contains 0.103 g of the insulin?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

**Exercise:****Problem:**

Assuming ideal solution behavior, what is the molar mass of a solution of 5.00 g of a compound in 25.00 g of carbon tetrachloride (bp  $76.8^\circ\text{C}$ ;  $K_b = 5.02^\circ\text{C}/m$ ) that boils at  $81.5^\circ\text{C}$  at 1 atm?

(a) Outline the steps necessary to answer the question.

(b) Solve the problem.

---

**Solution:**

(a) Determine the molal concentration from the change in boiling point and  $K_b$ ; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b)  $2.1 \times 10^2 \text{ g mol}^{-1}$

**Exercise:****Problem:**

A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by  $3.66^\circ\text{C}$ . Assuming ideal solution behavior, calculate the molar mass of the compound.

**Exercise:****Problem:**

A 1.0 *m* solution of HCl in benzene has a freezing point of  $0.4^\circ\text{C}$ . Is HCl an electrolyte in benzene? Explain.

---

**Solution:**

No. Pure benzene freezes at  $5.5^\circ\text{C}$ , and so the observed freezing point of this solution is depressed by  $\Delta T_f = 5.5 - 0.4 = 5.1^\circ\text{C}$ . The value computed, assuming no ionization of HCl, is  $\Delta T_f = (1.0 \text{ m})(5.14^\circ\text{C}/m) = 5.1^\circ\text{C}$ . Agreement of these values supports the assumption that HCl is not ionized.

**Exercise:****Problem:**

A solution contains 5.00 g of urea,  $\text{CO}(\text{NH}_2)_2$ , a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution (assuming ideal solution behavior)?

**Exercise:****Problem:**

A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at  $-1.94$  °C. Assuming ideal solution behavior, calculate the molar mass of the substance.

---

**Solution:**

$144 \text{ g mol}^{-1}$

**Exercise:****Problem:**

Arrange the following solutions in order by their decreasing freezing points: 0.1 *m*  $\text{Na}_3\text{PO}_4$ , 0.1 *m*  $\text{C}_2\text{H}_5\text{OH}$ , 0.01 *m*  $\text{CO}_2$ , 0.15 *m*  $\text{NaCl}$ , and 0.2 *m*  $\text{CaCl}_2$ .

**Exercise:****Problem:**

Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of  $\text{NaCl}$ , 0.020 mol of  $\text{Na}_2\text{SO}_4$ , and 0.030 mol of  $\text{MgCl}_2$ , assuming complete dissociation of these electrolytes and ideal solution behavior.

---

**Solution:**

$0.870$  °C

**Exercise:****Problem:**

How could you prepare a 3.08 *m* aqueous solution of glycerin,  $\text{C}_3\text{H}_8\text{O}_3$ ? Assuming ideal solution behavior, what is the freezing point of this solution?

**Exercise:****Problem:**

A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide,  $\text{CS}_2$  ( $K_b = 2.34$  °C/*m*). If the boiling point elevation was  $0.107$  °C, what is the formula of a sulfur molecule in carbon disulfide (assuming ideal solution behavior)?

---

**Solution:**

$\text{S}_8$



**Exercise:****Problem:**

In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI<sub>2</sub>?

**Exercise:****Problem:**

Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of  $1.32 \times 10^{-3}$  atm at 25 °C. Assuming ideal solution behavior, what is the molar mass of lysozyme?

---

**Solution:**

$$1.39 \times 10^4 \text{ g mol}^{-1}$$

**Exercise:****Problem:**

The osmotic pressure of a solution containing 7.0 g of insulin per liter is 23 torr at 25 °C. Assuming ideal solution behavior, what is the molar mass of insulin?

**Exercise:****Problem:**

The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, is required to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C (assuming ideal solution behavior)?

---

**Solution:**

$$54 \text{ g}$$

**Exercise:****Problem:**

Assuming ideal solution behavior, what is the freezing point of a solution of dibromobenzene, C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>, in 0.250 kg of benzene, if the solution boils at 83.5 °C?

**Exercise:****Problem:**

Assuming ideal solution behavior, what is the boiling point of a solution of NaCl in water if the solution freezes at -0.93 °C?

---

**Solution:**

$$100.26 \text{ °C}$$

**Exercise:****Problem:**

The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and  $K_b$  for ethanol is 1.20 °C/m. Assuming ideal solution behavior, what is the molecular formula of fructose?

**Exercise:****Problem:**

The vapor pressure of methanol, CH<sub>3</sub>OH, is 94 torr at 20 °C. The vapor pressure of ethanol, C<sub>2</sub>H<sub>5</sub>OH, is 44 torr at the same temperature.

- (a) Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.
- (b) Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapor pressure of methanol and of ethanol above the solution at 20 °C.
- (c) Calculate the mole fraction of methanol and of ethanol in the vapor above the solution.

---

**Solution:**

(a)  $X_{\text{CH}_3\text{OH}} = 0.590$ ;  $X_{\text{C}_2\text{H}_5\text{OH}} = 0.410$ ; (b) Vapor pressures are: CH<sub>3</sub>OH: 55 torr; C<sub>2</sub>H<sub>5</sub>OH: 18 torr; (c) CH<sub>3</sub>OH: 0.75; C<sub>2</sub>H<sub>5</sub>OH: 0.25

**Exercise:****Problem:**

The triple point of air-free water is defined as 273.16 K. Why is it important that the water be free of air?

**Exercise:****Problem:**

Meat can be classified as fresh (not frozen) even though it is stored at -1 °C. Why wouldn't meat freeze at this temperature?

---

**Solution:**

The ions and compounds present in the water in the beef lower the freezing point of the beef below -1 °C.

**Exercise:****Problem:**

An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C.  $K_f$  for camphor is 37.7 °C/m. Assuming ideal solution behavior, what is the molecular formula of the solute? Show your calculations.

**Exercise:****Problem:**

A sample of  $\text{HgCl}_2$  weighing 9.41 g is dissolved in 32.75 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$  ( $K_b = 1.20\text{ }^\circ\text{C}/m$ ). The boiling point elevation of the solution is  $1.27\text{ }^\circ\text{C}$ . Is  $\text{HgCl}_2$  an electrolyte in ethanol? Show your calculations.

**Solution:**

$$\Delta bp = K_b m = (1.20\text{ }^\circ\text{C}/m) \left( \frac{9.41\text{ g} \times \frac{1\text{ mol HgCl}_2}{271.496\text{ g}}}{0.03275\text{ kg}} \right) = 1.27\text{ }^\circ\text{C}$$

The observed change equals the theoretical change; therefore, no dissociation occurs.

**Exercise:****Problem:**

A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about  $-1.4\text{ }^\circ\text{C}$ . Assuming ideal solution behavior, what is the formula of the salt? Show your calculations.

**Glossary**

boiling point elevation

elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant

the proportionality constant in the equation relating boiling point elevation to solute molality;  
also known as the ebullioscopic constant

colligative property

property of a solution that depends only on the concentration of a solute species

crenation

process whereby biological cells become shriveled due to loss of water by osmosis

freezing point depression

lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant

(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

hemolysis

rupture of red blood cells due to the accumulation of excess water by osmosis

hypertonic

of greater osmotic pressure

hypotonic  
of less osmotic pressure

ion pair  
solvated anion/cation pair held together by moderate electrostatic attraction

isotonic  
of equal osmotic pressure

molality ( $m$ )  
a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

osmosis  
diffusion of solvent molecules through a semipermeable membrane

osmotic pressure ( $\Pi$ )  
opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Raoult's law  
the relationship between a solution's vapor pressure and the vapor pressures and concentrations of its components

semipermeable membrane  
a membrane that selectively permits passage of certain ions or molecules

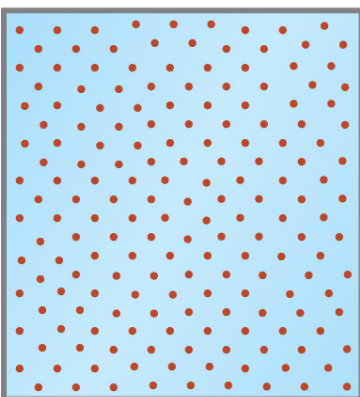
van't Hoff factor ( $i$ )  
the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

## Colloids

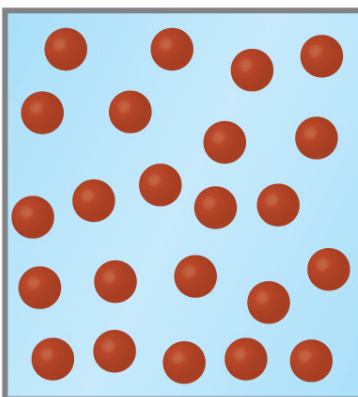
By the end of this section, you will be able to:

- Describe the composition and properties of colloidal dispersions
- List and explain several technological applications of colloids

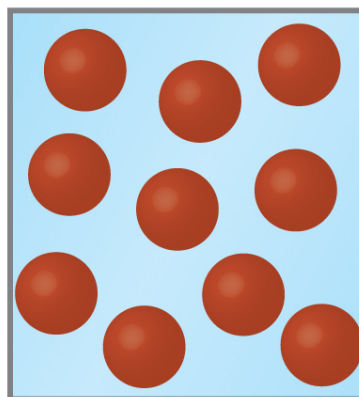
As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These **suspensions** are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, a solution is a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. Another class of mixtures called **colloids** (or **colloidal dispersions**) exhibit properties intermediate between those of suspensions and solutions ([\[link\]](#)). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.



(a)



(b)



(c)

(a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are much larger but remain dispersed and do not settle. (c) A suspension, such as

mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

The particles in a colloid are large enough to scatter light, a phenomenon called the **Tyndall effect**. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in [\[link\]](#). Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.



The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: “Bahman”/Wikimedia Commons)

The term “colloid”—from the Greek words *kolla*, meaning “glue,” and *eidos*, meaning “like”—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as “solute” and “solvent,” the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the **dispersed phase** and the substance or solution throughout which the particulate is dispersed is called the **dispersion medium**. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in [\[link\]](#).

Examples of Colloidal Systems			
Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion
liquid	solid	jellies, gels, pearl, opal (H <sub>2</sub> O in SiO <sub>2</sub> )	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

## Preparation of Colloidal Systems

Colloids are prepared by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

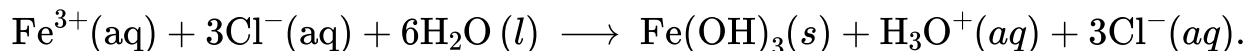
1. Dispersion methods: breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

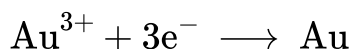
An **emulsion** may be prepared by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an **emulsifying agent**, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein serving as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. A red colloidal suspension of iron(III) hydroxide may be prepared by mixing a concentrated solution of iron(III) chloride with hot water:



**Equation:**

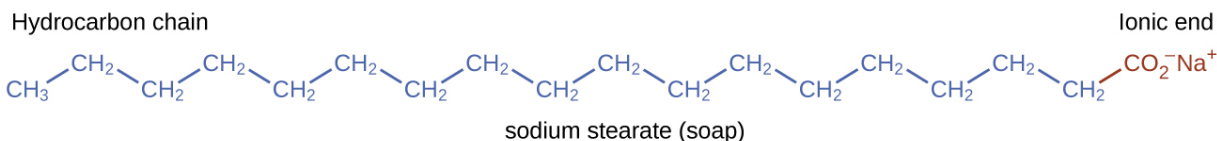
A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

**Equation:**

Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

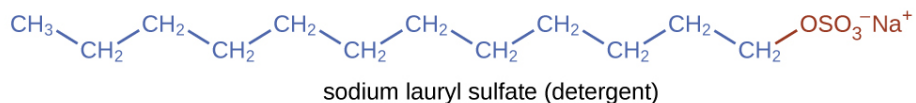
**Soaps and Detergents**

Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate,  $\text{K}_2\text{CO}_3$ , from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called *soaps*. The sodium salt of stearic acid, sodium stearate, has the formula  $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$  and contains an uncharged nonpolar hydrocarbon chain, the  $\text{C}_{17}\text{H}_{35}$ — unit, and an ionic carboxylate group, the  $\text{—CO}_2^{-}$  unit ([link](#)).



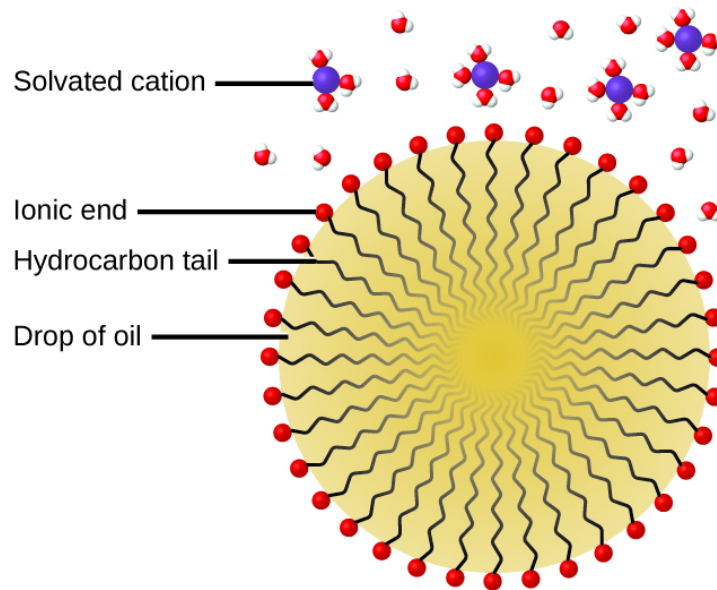
Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

*Detergents* (soap substitutes) also contain nonpolar hydrocarbon chains, such as  $\text{C}_{12}\text{H}_{25}$ —, and an ionic group, such as a sulfate— $\text{OSO}_3^-$ , or a sulfonate— $\text{SO}_3^-$  ([\[link\]](#)). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.



Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in [\[link\]](#). As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed **amphiphilic** since they have both a hydrophobic (“water-fearing”) part and a hydrophilic (“water-loving”) part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.



This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.

**Note:**

**Deepwater Horizon Oil Spill**

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi began the largest marine oil spill in the history of the petroleum industry. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water's surface. The well was finally declared sealed on September 19, 2010.

Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water's surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to removal of the oil, attempts were also made to lessen its environmental impact by rendering it "soluble" (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the

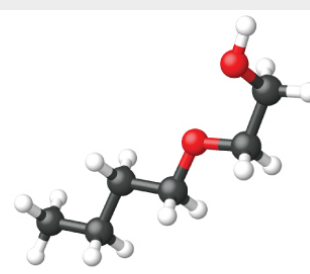
spill. Corexit 9527 contains 2-butoxyethanol ( $\text{C}_6\text{H}_{14}\text{O}_2$ ), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion ([\[link\]](#)). While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it introduces the possibility of long-term effects resulting from the introduction of the complex and potential toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration (visit this [website](#) for additional details).



(a)



(b)



(c)

(a) This NASA satellite image shows the oil slick from the Deepwater Horizon spill. (b) A US Air Force plane sprays Corexit, a dispersant. (c) The molecular structure of 2-butoxyethanol is shown. (credit a: modification of work by “NASA, FT2, demis.nl”/Wikimedia Commons; credit b: modification of work by “NASA/MODIS Rapid Response Team”/Wikimedia Commons)

## Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same

sign. This helps keep them dispersed because particles containing like charges repel each other.

The charged nature of some colloidal particles may be exploited to remove them from a variety of mixtures. For example, the particles comprising smoke are often colloidally dispersed and electrically charged. Frederick Cottrell, an American chemist, developed a process to remove these particles. The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust ([\[link\]](#)). This is one of the important methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable products from the smoke and flue dust of smelters, furnaces, and kilns. There are also similar electrostatic air filters designed for home use to improve indoor air quality.

**Note:**

Frederick Gardner Cottrell



(a)

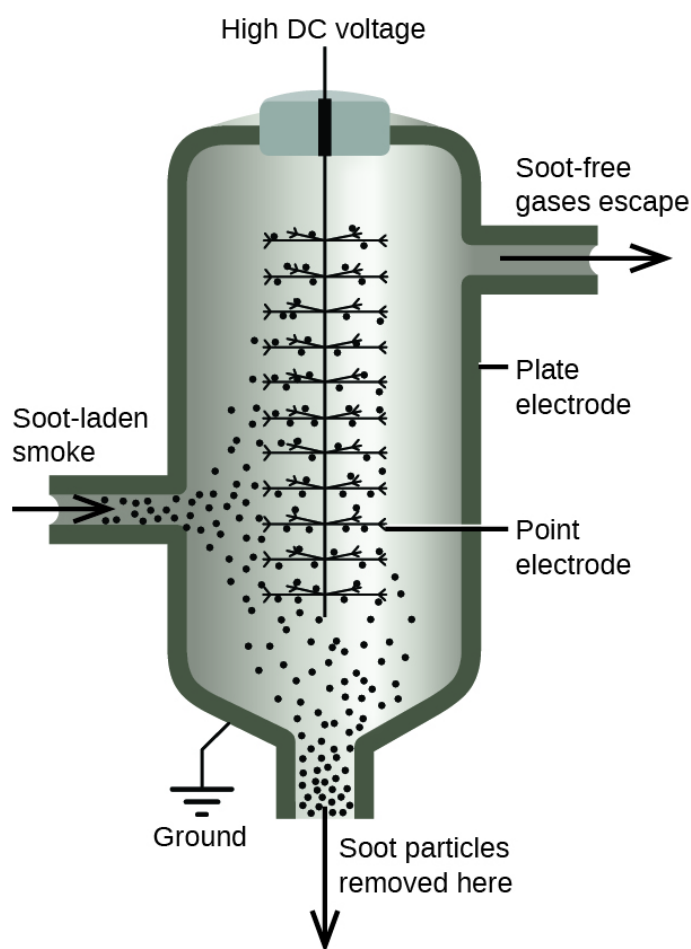


(b)

(a) Frederick Cottrell developed (b) the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. (credit b: modification of work by “SpLot”/Wikimedia Commons)

Born in Oakland, CA, in 1877, Frederick Cottrell devoured textbooks as if they were novels and graduated from high school at the age of 16. He then entered the

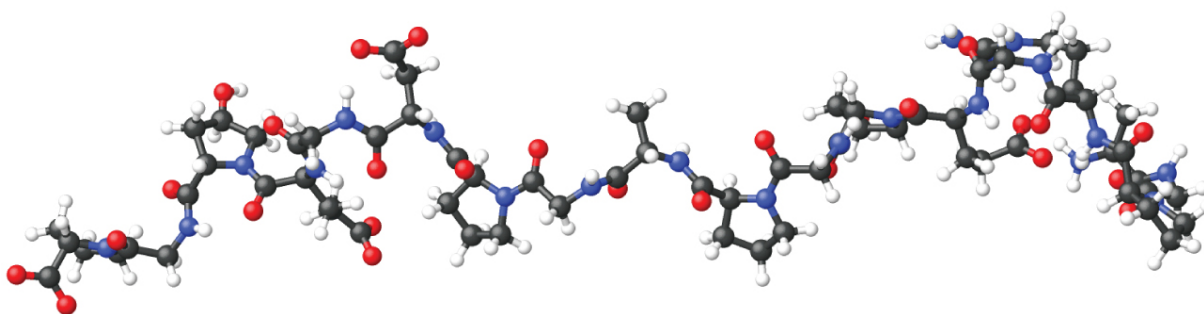
University of California (UC), Berkeley, completing a Bachelor's degree in three years. He saved money from his \$1200 annual salary as a chemistry teacher at Oakland High School to fund his studies in chemistry in Berlin with Nobel prize winner Jacobus Henricus van't Hoff, and in Leipzig with Wilhelm Ostwald, another Nobel awardee. After earning his PhD in physical chemistry, he returned to the United States to teach at UC Berkeley. He also consulted for the DuPont Company, where he developed the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. Cottrell used the proceeds from his invention to fund a nonprofit research corporation to finance scientific research.



In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust.

## Gels

Gelatin desserts, such as Jell-O, are a type of colloid ([link](#)). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools, yielding an extremely viscous body known as a **gel**. A gel is a colloidal dispersion of a liquid phase throughout a solid phase. It appears that the fibers of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium.



Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavors is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo)

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium

silicate. Canned Heat is a flammable gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Key Concepts and Summary

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.

Solution:

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air
fog	water	air
pearl	water	calcium carbonate (CaCO <sub>3</sub> )



Colloidal System	Dispersed Phase	Dispersion Medium
whipped cream	air	cream
floating soap	air	soap
jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide ( $\text{Cr}_2\text{O}_3$ )	aluminum oxide ( $\text{Al}_2\text{O}_3$ )

**Exercise:**

**Problem:**

Distinguish between dispersion methods and condensation methods for preparing colloidal systems.

**Exercise:**

**Problem:**

How do colloids differ from solutions with regard to dispersed particle size and homogeneity?

**Solution:**

Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.

**Exercise:**

**Problem:** Explain the cleansing action of soap.

**Exercise:****Problem:**

How can it be demonstrated that colloidal particles are electrically charged?

---

**Solution:**

If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

**Glossary****amphiphilic**

molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

**colloid**

(also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

**dispersion medium**

solid, liquid, or gas in which colloidal particles are dispersed

**dispersed phase**

substance present as relatively large solid or liquid particles in a colloid

**emulsifying agent**

amphiphilic substance used to stabilize the particles of some emulsions

**emulsion**

colloid formed from immiscible liquids

**gel**

colloidal dispersion of a liquid in a solid

**suspension**

heterogeneous mixture in which relatively large component particles are temporarily dispersed but settle out over time

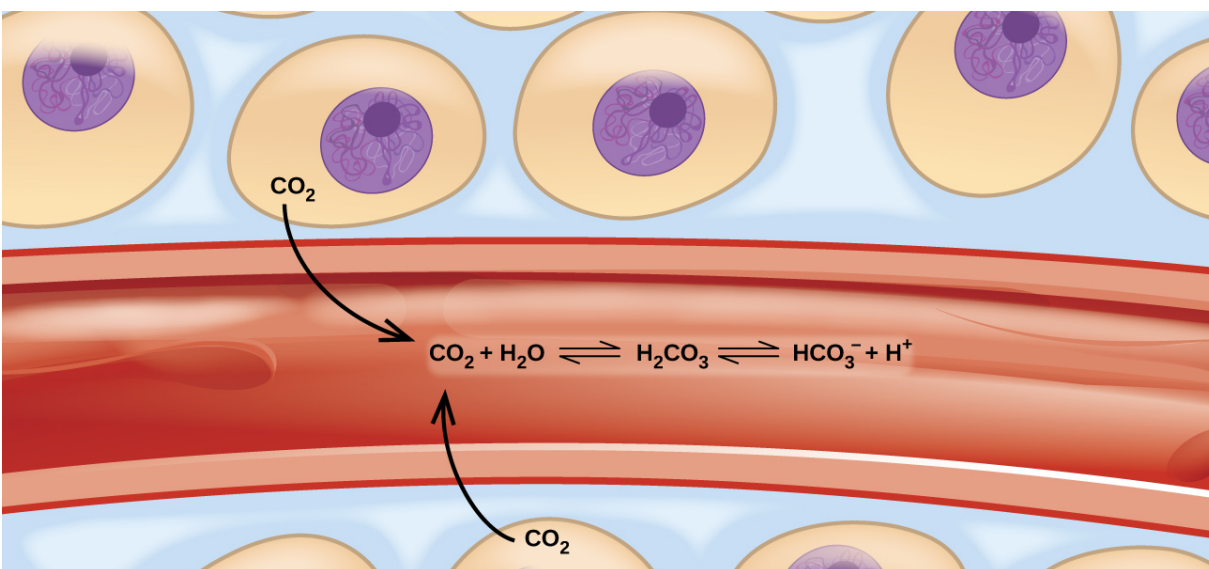
Tyndall effect  
scattering of visible light by a colloidal dispersion

## Introduction

class="introduction"

- Chemical Equilibria
- Equilibrium Constants
- Shifting Equilibria: Le Châtelier's Principle
- Equilibrium Calculations

Transport  
of carbon  
dioxide in  
the body  
involves  
several  
reversible  
chemical  
reactions,  
including  
hydrolysi  
s and acid  
ionization  
(among  
others).



Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as *equilibrium*, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples (see [\[link\]](#)). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

We now have a good understanding of chemical and physical change that allow us to determine, for any given process:

1. Whether the process is endothermic or exothermic
2. Whether the process is accompanied by an increase of decrease in entropy
3. Whether a process will be spontaneous, non-spontaneous, or what we have called an equilibrium process

Recall that when the value  $\Delta G$  for a reaction is zero, we consider there to be no free energy change—that is, no free energy available to do useful work. Does this mean a reaction where  $\Delta G = 0$  comes to a complete halt? No, it does not. Just as a liquid exists in equilibrium with its vapor in a closed container, where the rates of evaporation and condensation are equal, there is a connection to the state of equilibrium for a phase change or a chemical reaction. That is, at equilibrium, the forward and reverse rates of reaction are equal. We will develop that concept and extend it to a relationship between equilibrium and free energy later in this chapter.

In the explanation that follows, we will use the term  $Q$  to refer to any reactant or product concentration or pressure. When the concentrations or pressure of reactants and products are at equilibrium, the term  $K$  will be used. This will be more clearly explained as we go along in this chapter.

Now we will consider the connection between the free energy change and the equilibrium constant. The fundamental relationship is:

$\Delta G^\circ = -RT\ln K$ —this can be for  $K_c$  or  $K_p$  (and we will see later, any equilibrium constant we encounter).

We also know that the form of  $K$  can be used in non-equilibrium conditions as the reaction quotient,  $Q$ . The defining relationship here is

**Equation:**

$$\Delta G = \Delta G^\circ + RT\ln Q$$

Without the superscript, the value of  $\Delta G$  can be calculated for any set of concentrations.

Note that since  $Q$  is a mass-action reaction of productions/reactants, as a reaction proceeds from left to right, product concentrations increase as reactant concentrations decrease, until  $Q = K$ , and at which time  $\Delta G$  becomes zero:

$0 = \Delta G^\circ + RT\ln K$ , a relationship that reduces to our defining connection between  $Q$  and  $K$ .

Thus, we can see clearly that as a reaction moves toward equilibrium, the value of  $\Delta G$  goes to zero.

Now, think back to the connection between the signs of  $\Delta G^\circ$  and  $\Delta H^\circ$

$\Delta H^\circ$	$\Delta S^\circ$	Result
Negative	Positive	Always spontaneous
Positive	Negative	Never spontaneous
Positive	Positive	Spontaneous at high temperatures
Negative	Negative	Spontaneous at low temperatures

Only in the last two cases is there a point at which the process swings from spontaneous to non-spontaneous (or the reverse); in these cases, the process must pass through equilibrium when the change occurs. The concept of the connection between the free energy change and the equilibrium constant is an important one that we will expand upon in future sections. The fact that the change in free energy for an equilibrium process is zero, and that displacement of a process from that zero point results in a drive to re-establish equilibrium is fundamental to understanding the behavior of chemical reactions and phase changes.

## Chemical Equilibria

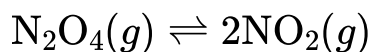
By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

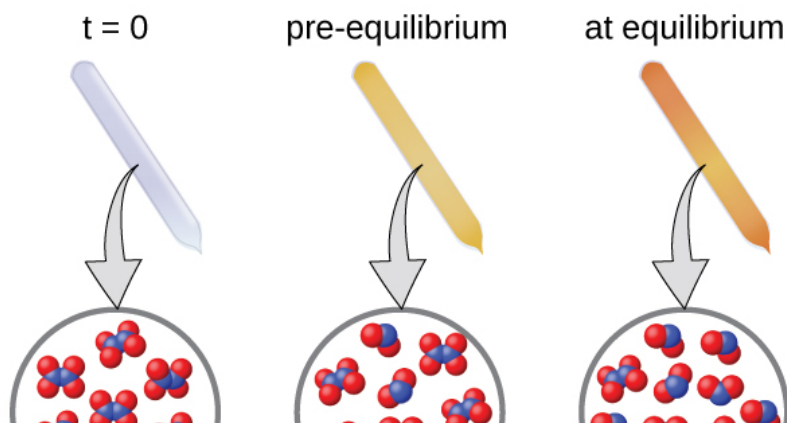
The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of “reactant” and “product,” a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

[\[link\]](#) illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

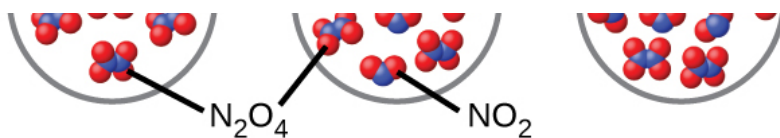
**Equation:**



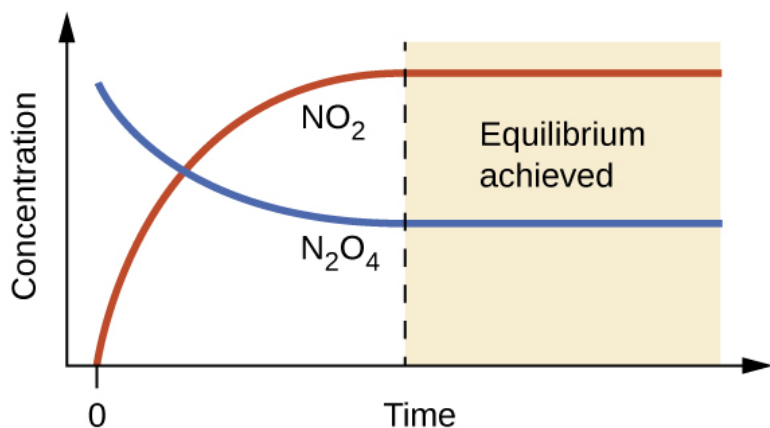
Note that a special double arrow is used to emphasize the reversible nature of the reaction.



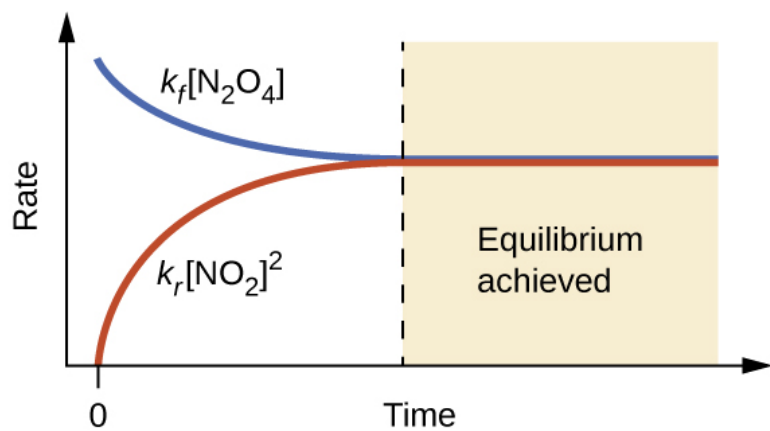




(a)



(b)



(c)

(a) A sealed tube containing colorless  $\text{N}_2\text{O}_4$  darkens as it decomposes to yield brown  $\text{NO}_2$ .  
 (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

**Equation:**

$$\text{rate}_f = k_f[\text{N}_2\text{O}_4]$$

**Equation:**

$$\text{rate}_r = k_r[\text{NO}_2]^2$$

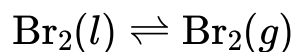
As the reaction begins ( $t = 0$ ), the concentration of the  $\text{N}_2\text{O}_4$  reactant is finite and that of the  $\text{NO}_2$  product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes,  $\text{N}_2\text{O}_4$  is consumed and its concentration falls, while  $\text{NO}_2$  is produced and its concentration increases ([\[link\]b](#)). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate ([\[link\]c](#)). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of [\[link\]b](#) and [\[link\]c](#)). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not “stopped,” but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.



A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

**Equation:**



When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will

commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in [\[link\]](#).



A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: <http://images-of-elements.com/bromine.php>)

## Key Concepts and Summary

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species.

## Chemistry End of Chapter Exercises

### Exercise:

**Problem:** What does it mean to describe a reaction as “reversible”?

---

### Solution:

The reaction can proceed in both the forward and reverse directions.

### Exercise:

### Problem:

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

### Exercise:

### Problem:

If a reaction is reversible, when can it be said to have reached equilibrium?

---

### Solution:

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to proceed, but at equal rates.

**Exercise:**

**Problem:**

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

**Exercise:**

**Problem:**

If the concentrations of products and reactants are equal, is the system at equilibrium?

---

**Solution:**

Not necessarily. A system at equilibrium is characterized by *constant* reactant and product concentrations, but the values of the reactant and product concentrations themselves need not be equal.

## Glossary

**equilibrium**

state of a reversible reaction in which the forward and reverse processes occur at equal rates

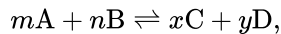
**reversible reaction**

chemical reaction that can proceed in both the forward and reverse directions under given conditions

## Equilibrium Constants

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient ( $Q$ )**. For a reversible reaction described by

**Equation:**



the reaction quotient is derived directly from the stoichiometry of the balanced equation as

**Equation:**

$$Q_c = \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n},$$

where the subscript  $c$  denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

**Equation:**

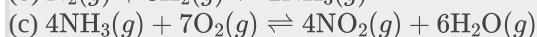
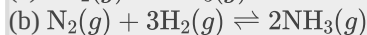
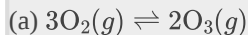
$$Q_p = \frac{P_{\text{C}x} P_{\text{D}y}}{P_{\text{A}m} P_{\text{B}n}}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing  $Q$ . In most cases, this will introduce only modest errors in calculations involving reaction quotients.

### Example:

#### Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:



#### Solution

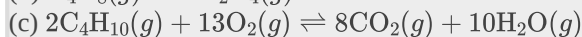
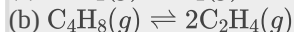
(a)  $Q_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$

(b)  $Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

(c)  $Q_c = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$

#### Check Your Learning

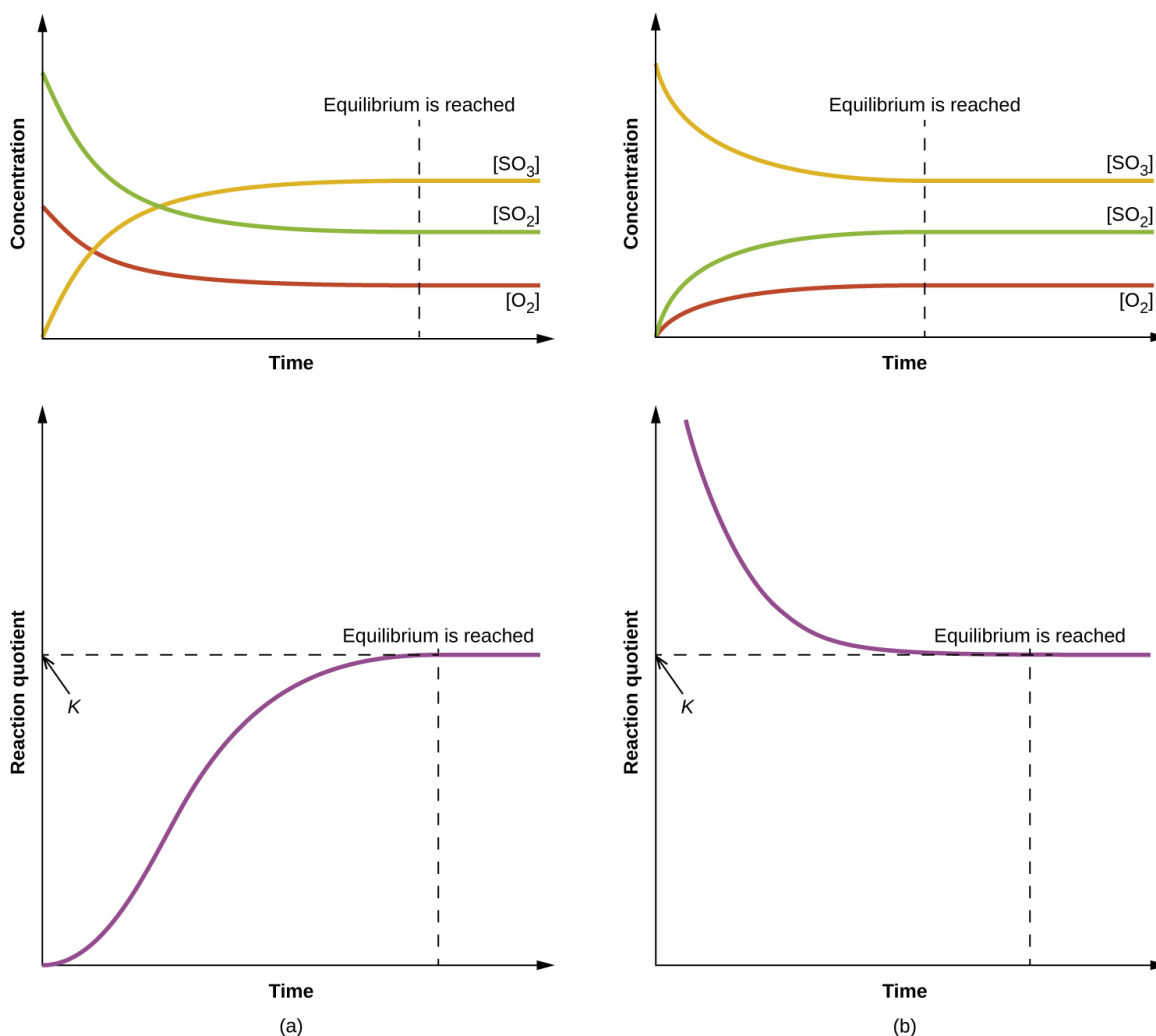
Write the concentration-based reaction quotient expression for each of the following reactions:



#### Note:

#### Answer:

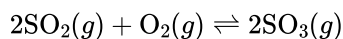
(a)  $Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$ ; (b)  $Q_c = \frac{[\text{C}_2\text{H}_4]^2}{[\text{C}_4\text{H}_8]}$ ; (c)  $Q_c = \frac{[\text{CO}_2]^8 [\text{H}_2\text{O}]^{10}}{[\text{C}_4\text{H}_{10}]^2 [\text{O}_2]^{13}}$



Changes in concentrations and  $Q_c$  for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of  $Q$  varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

**Equation:**



Two different experimental scenarios are depicted in [\[link\]](#), one in which this reaction is initiated with a mixture of reactants only,  $\text{SO}_2$  and  $\text{O}_2$ , and another that begins with only product,  $\text{SO}_3$ . For the reaction that begins with a mixture of reactants only,  $Q$  is initially equal to zero:

**Equation:**



$$Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{0^2}{[\text{SO}_2]^2 [\text{O}_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of  $Q_c$ ), product concentration increases (as does the numerator of  $Q_c$ ), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of  $Q_c$ .

If the reaction begins with only product present, the value of  $Q_c$  is initially undefined (immeasurably large, or infinite):

**Equation:**

$$Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{[\text{SO}_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of  $Q_c$  decrease with time, the reactant concentrations and the denominator of  $Q_c$  increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of  $Q$  exhibited by a system at equilibrium is called the **equilibrium constant,  $K$** :

**Equation:**

$$K \equiv Q \text{ at equilibrium}$$

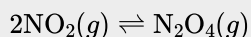
Comparison of the data plots in [link](#) shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**: At a given temperature, the reaction quotient for a system at equilibrium is constant.

### Example:

#### Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

**Equation:**



When 0.10 mol  $\text{NO}_2$  is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium,  $[\text{NO}_2] = 0.016 \text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.042 \text{ M}$ .

(a) What is the value of the reaction quotient before any reaction occurs?

(b) What is the value of the equilibrium constant for the reaction?

#### Solution

As for all equilibrium calculations in this text, use the simplified equations for  $Q$  and  $K$  and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed,  $[\text{NO}_2] = \frac{0.10 \text{ mol}}{1.0 \text{ L}} = 0.10 \text{ M}$ , and  $[\text{N}_2\text{O}_4] = 0 \text{ M}$ . Thus,

**Equation:**

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium,  $K_c = Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2$ . The equilibrium constant is  $1.6 \times 10^2$ .

**Check Your Learning**

For the reaction  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ , the concentrations at equilibrium are  $[\text{SO}_2] = 0.90\text{ M}$ ,  $[\text{O}_2] = 0.35\text{ M}$ , and  $[\text{SO}_3] = 1.1\text{ M}$ . What is the value of the equilibrium constant,  $K_c$ ?

**Note:**

**Answer:**

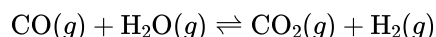
$K_c = 4.3$

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large  $K$  will reach equilibrium when most of the reactant has been converted to product, whereas a small  $K$  indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of  $K$  does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing  $Q$  to  $K$  for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below:

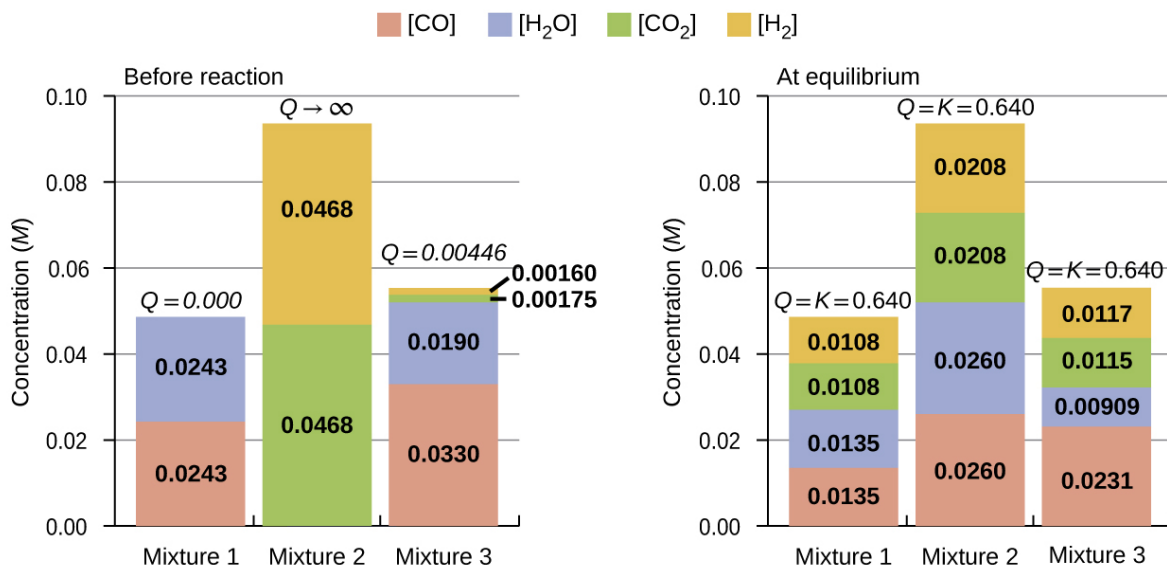
**Equation:**



$$K_c = 0.640$$

$$T = 800\text{ }^\circ\text{C}$$

The bar charts in [\[link\]](#) represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.



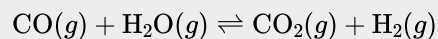
Compositions of three mixtures before ( $Q_c \neq K_c$ ) and after ( $Q_c = K_c$ ) equilibrium is established for the reaction  $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$ .

**Example:**

**Predicting the Direction of Reaction**

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

**Equation:**



**Equation:**

$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[\text{CO}]_i$	0.020 M	0.011 M	0.0094 M
$[\text{H}_2\text{O}]_i$	0.020 M	0.0011 M	0.0025 M
$[\text{CO}_2]_i$	0.0040 M	0.037 M	0.0015 M
$[\text{H}_2]_i$	0.0040 M	0.046 M	0.0076 M

**Solution**

Experiment 1:

**Equation:**

$$Q_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040.$$

$$Q_c < K_c \quad (0.040 < 0.64)$$

The reaction will proceed in the forward direction.

Experiment 2:

**Equation:**

$$Q_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$$Q_c > K_c \quad (140 > 0.64)$$

The reaction will proceed in the reverse direction.

Experiment 3:

**Equation:**

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$$Q_c < K_c \quad (0.48 < 0.64)$$

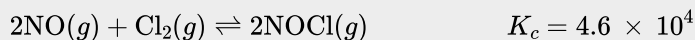
The reaction will proceed in the forward direction.

### Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

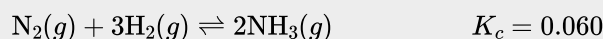
(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl<sub>2</sub>(g), and 0.500 mol of NOCl:

**Equation:**



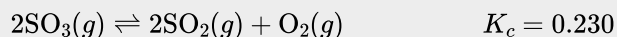
(b) A 5.0-L flask containing 17 g of NH<sub>3</sub>, 14 g of N<sub>2</sub>, and 12 g of H<sub>2</sub>:

**Equation:**



(c) A 2.00-L flask containing 230 g of SO<sub>3</sub>(g):

**Equation:**



**Note:**

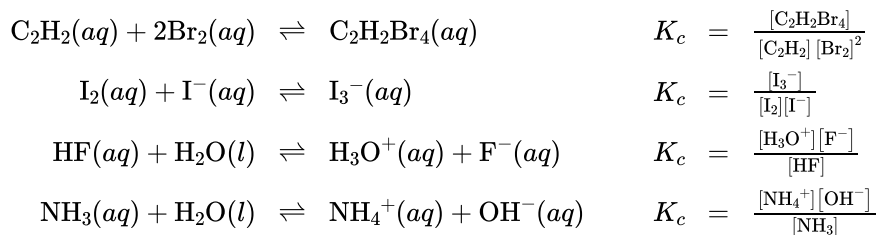
**Answer:**

(a)  $Q_c = 6.45 \times 10^3$ , forward. (b)  $Q_c = 0.23$ , reverse. (c)  $Q_c = 0$ , forward.

## Homogeneous Equilibria

A **homogeneous equilibrium** is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

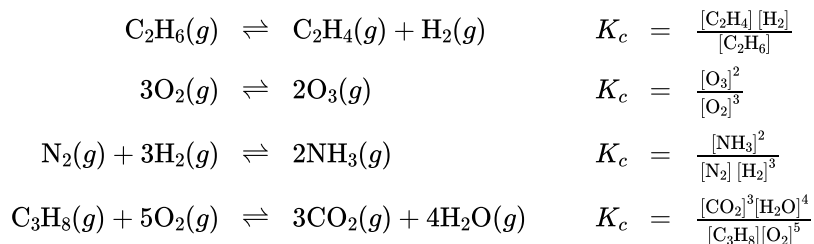
**Equation:**



These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the  $Q$  (or  $K$ ) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

The equilibria below all involve gas-phase solutions:

**Equation:**



For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations ( $K_c$ ) or partial pressures ( $K_p$ ) of the reactants and products. A relation between these two  $K$  values may be simply derived from the ideal gas equation and the definition of molarity:

**Equation:**

$$PV = nRT$$

**Equation:**

$$P = \left(\frac{n}{V}\right)RT$$

**Equation:**

$$= MRT$$

where  $P$  is partial pressure,  $V$  is volume,  $n$  is molar amount,  $R$  is the gas constant,  $T$  is temperature, and  $M$  is molar concentration.

For the gas-phase reaction  $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$ :

**Equation:**

$$K_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$$

**Equation:**

$$= \frac{([\text{C}] \times RT)^x([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m([\text{B}] \times RT)^n}$$

**Equation:**

$$= \frac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^m[\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

**Equation:**

$$= K_c(RT)^{(x+y)-(m+n)}$$

**Equation:**

$$= K_c(RT)^{\Delta n}$$

And so, the relationship between  $K_c$  and  $K_p$  is

**Equation:**

$$K_P = K_c(RT)^{\Delta n}$$

where  $\Delta n$  is the difference in the molar amounts of product and reactant gases, in this case:

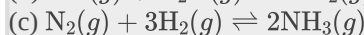
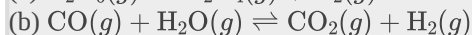
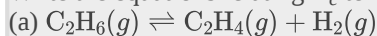
**Equation:**

$$\Delta n = (x+y) - (m+n)$$

**Example:**

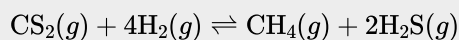
**Calculation of  $K_P$**

Write the equations relating  $K_c$  to  $K_P$  for each of the following reactions:



(d)  $K_c$  is equal to 0.28 for the following reaction at 900 °C:

**Equation:**



What is  $K_P$  at this temperature?

**Solution**

(a)  $\Delta n = (2) - (1) = 1$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$$

(b)  $\Delta n = (2) - (2) = 0$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$$

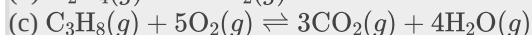
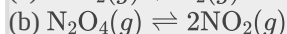
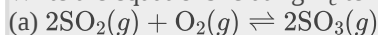
(c)  $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$

(d)  $K_P = K_c (RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

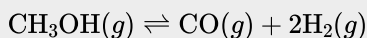
**Check Your Learning**

Write the equations relating  $K_c$  to  $K_P$  for each of the following reactions:



(d) At 227 °C, the following reaction has  $K_c = 0.0952$ :

**Equation:**



What would be the value of  $K_P$  at this temperature?

**Note:**

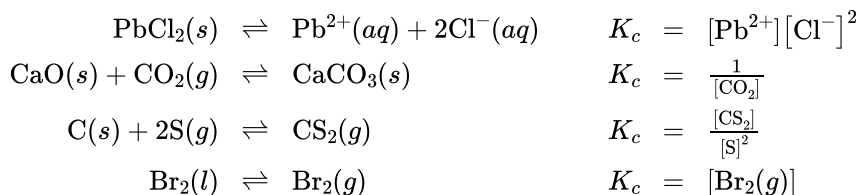
**Answer:**

(a)  $K_P = K_c (RT)^{-1}$ ; (b)  $K_P = K_c (RT)$ ; (c)  $K_P = K_c (RT)$ ; (d) 160 or  $1.6 \times 10^2$

## Heterogeneous Equilibria

A **heterogeneous equilibrium** involves reactants and products in two or more different phases, as illustrated by the following examples:

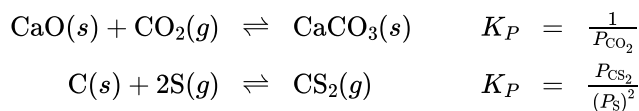
**Equation:**



Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so  $K_p$  expressions may also be written:

**Equation:**



## Key Concepts and Summary

The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient,  $Q$ . For a reaction at equilibrium, the composition is constant, and  $Q$  is called the equilibrium constant,  $K$ .

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases.

## Key Equations

$Q_c = \frac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^m[\text{B}]^n}$	for the reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$
$Q_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$	for the reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$
$P = MRT$	
$K_c = Q_c$ at equilibrium	
$K_P = Q_P$ at equilibrium	
$K_P = K_c (RT)^{\Delta n}$	

## Chemistry End of Chapter Exercises

**Exercise:****Problem:**

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

**Exercise:****Problem:**

Explain why an equilibrium between  $\text{Br}_2(l)$  and  $\text{Br}_2(g)$  would not be established if the container were not a closed vessel shown in [\[link\]](#).

---

**Solution:**

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the  $\text{Br}_2$  vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

**Exercise:****Problem:**

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure  $\text{NO}_2$  or with pure  $\text{N}_2\text{O}_4$ ?  
 $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$

**Exercise:****Problem:**

Among the solubility rules previously discussed is the statement: All chlorides are soluble except  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$ , and  $\text{CuCl}$ .

(a) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{PbCl}_2(s)$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

---

**Solution:**

(a)  $K_c = [\text{Ag}^+][\text{Cl}^-] < 1$ .  $\text{AgCl}$  is insoluble; thus, the concentrations of ions are much less than 1 M; (b)  $K_c = \frac{1}{[\text{Pb}^{2+}][\text{Cl}^-]^2} > 1$  because  $\text{PbCl}_2$  is insoluble and formation of the solid will reduce the concentration of ions to a low level ( $< 1$  M).

**Exercise:****Problem:**

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation  $3\text{Ba}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \rightleftharpoons \text{Ba}_3(\text{PO}_4)_2(s)$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

**Exercise:**



**Problem:**

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:  $3\text{C}_2\text{H}_2(g) \rightleftharpoons \text{C}_6\text{H}_6(g)$ . Which value of  $K_c$  would make this reaction most useful commercially?  $K_c \approx 0.01$ ,  $K_c \approx 1$ , or  $K_c \approx 10$ . Explain your answer.

---

**Solution:**

Since  $K_c = \frac{[\text{C}_6\text{H}_6]}{[\text{C}_2\text{H}_2]^3}$ , a value of  $K_c \approx 10$  means that  $\text{C}_6\text{H}_6$  predominates over  $\text{C}_2\text{H}_2$ . In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

**Exercise:****Problem:**

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation  $\text{KI}(aq) + \text{I}_2(aq) \rightleftharpoons \text{KI}_3(aq)$  give the same expression for the reaction quotient.  $\text{KI}_3$  is composed of the ions  $\text{K}^+$  and  $\text{I}_3^-$ .

**Exercise:****Problem:**

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$  for a titration reaction?

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**Solution:**

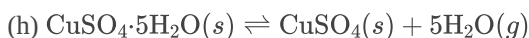
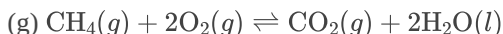
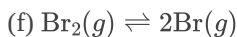
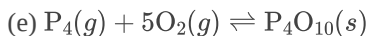
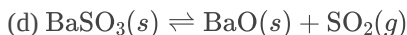
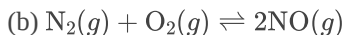
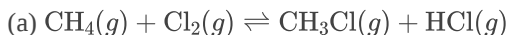
$$K_c > 1$$

**Exercise:****Problem:**

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$  for a useful precipitation reaction?

**Exercise:**

**Problem:** Write the mathematical expression for the reaction quotient,  $Q_c$ , for each of the following reactions:

**Solution:**

$$(a) Q_c = \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]}; (b) Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}; (c) Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}; (d) Q_c = [\text{SO}_2]; (e) Q_c = \frac{1}{[\text{P}_4][\text{O}_2]^5}; (f) Q_c = \frac{[\text{Br}]^2}{[\text{Br}_2]}; (g) Q_c = \frac{[\text{CO}_2]}{[\text{CH}_4][\text{O}_2]^2}; (h) Q_c = [\text{H}_2\text{O}]^5$$

**Exercise:**

**Problem:** Write the mathematical expression for the reaction quotient,  $Q_c$ , for each of the following reactions:

- (a)  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$   
 (b)  $4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$   
 (c)  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$   
 (d)  $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$   
 (e)  $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$   
 (f)  $2\text{Pb}(\text{NO}_3)_2(s) \rightleftharpoons 2\text{PbO}(s) + 4\text{NO}_2(g) + \text{O}_2(g)$   
 (g)  $2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(l)$   
 (h)  $\text{S}_8(g) \rightleftharpoons 8\text{S}(g)$

**Exercise:**

**Problem:**

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

- |  |  |
|--|--|
| (a) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$  | $K_c = 17; [\text{NH}_3] = 0.20 M, [\text{N}_2] = 1.00 M, [\text{H}_2] = 1.00 M$                                   |
| (b) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$  | $K_P = 6.8 \times 10^4; \text{NH}_3 = 3.0 \text{ atm}, \text{N}_2 = 2.0 \text{ atm}, \text{H}_2 = 1.0 \text{ atm}$ |
| (c) $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ | $K_c = 0.230; [\text{SO}_3] = 0.00 M, [\text{SO}_2] = 1.00 M, [\text{O}_2] = 1.00 M$                               |
| (d) $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ | $K_P = 16.5; \text{SO}_3 = 1.00 \text{ atm}, \text{SO}_2 = 1.00 \text{ atm}, \text{O}_2 = 1.00 \text{ atm}$        |
| (e) $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$  | $K_c = 4.6 \times 10^4; [\text{NO}] = 1.00 M, [\text{Cl}_2] = 1.00 M, [\text{NOCl}] = 0 M$                         |
| (f) $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$     | $K_P = 0.050; \text{NO} = 10.0 \text{ atm}, \text{N}_2 = \text{O}_2 = 5 \text{ atm}$                               |

**Solution:**

- (a)  $Q_c$  25 proceeds left; (b)  $Q_P$  0.22 proceeds right; (c)  $Q_c$  undefined proceeds left; (d)  $Q_P$  1.00 proceeds right; (e)  $Q_P$  0 proceeds right; (f)  $Q_c$  4 proceeds left

**Exercise:**

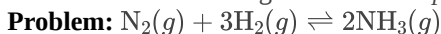
**Problem:**

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

- |  |   |
|--|---|
| (a) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$  | $K_c = 17$ ; $[\text{NH}_3] = 0.50\text{ M}$ , $[\text{N}_2] = 0.15\text{ M}$ , $[\text{H}_2] = 0.12\text{ M}$            |
| (b) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$  | $K_P = 6.8 \times 10^4$ ; $\text{NH}_3 = 2.00\text{ atm}$ , $\text{N}_2 = 10.00\text{ atm}$ , $\text{H}_2 = 10.00$        |
| (c) $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ | $K_c = 0.230$ ; $[\text{SO}_3] = 2.00\text{ M}$ , $[\text{SO}_2] = 2.00\text{ M}$ , $[\text{O}_2] = 2.00\text{ M}$        |
| (d) $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ | $K_P = 6.5\text{ atm}$ ; $\text{SO}_2 = 1.00\text{ atm}$ , $\text{O}_2 = 1.130\text{ atm}$ , $\text{SO}_3 = 0\text{ atm}$ |
| (e) $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$  | $K_P = 2.5 \times 10^3$ ; $\text{NO} = 1.00\text{ atm}$ , $\text{Cl}_2 = 1.00\text{ atm}$ , $\text{NOCl} = 0$             |
| (f) $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$     | $K_c = 0.050$ ; $[\text{N}_2] = 0.100\text{ M}$ , $[\text{O}_2] = 0.200\text{ M}$ , $[\text{NO}] = 1.00\text{ M}$         |

**Exercise:**

The following reaction has  $K_P = 4.50 \times 10^{-5}$  at 720 K.



If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium?  $P(\text{NH}_3) = 93\text{ atm}$ ,  $P(\text{N}_2) = 48\text{ atm}$ , and  $P(\text{H}_2) = 52\text{ atm}$

**Solution:**

The system will shift toward the reactants to reach equilibrium.

**Exercise:**

**Problem:**

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?



$[\text{SO}_2\text{Cl}_2] = 0.12\text{ M}$ ,  $[\text{Cl}_2] = 0.16\text{ M}$  and  $[\text{SO}_2] = 0.050\text{ M}$ .  $K_c$  for the reaction is 0.078.

**Exercise:**

**Problem:**

Which of the systems described in [\[link\]](#) are homogeneous equilibria? Which are heterogeneous equilibria?

**Solution:**

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

**Exercise:**

**Problem:**

Which of the systems described in [\[link\]](#) are homogeneous equilibria? Which are heterogeneous equilibria?

**Exercise:**

**Problem:**

For which of the reactions in [\[link\]](#) does  $K_c$  (calculated using concentrations) equal  $K_P$  (calculated using pressures)?

**Solution:**

This situation occurs in (a) and (b).

**Exercise:**

**Problem:**

For which of the reactions in [\[link\]](#) does  $K_c$  (calculated using concentrations) equal  $K_P$  (calculated using pressures)?

**Exercise:**

**Problem:** Convert the values of  $K_c$  to values of  $K_P$  or the values of  $K_P$  to values of  $K_c$ .

- |   |  |
|---|--|
| (a) $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$   | $K_c = 0.50$ at $400^\circ\text{C}$                |
| (b) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  | $K_c = 50.2$ at $448^\circ\text{C}$                |
| (c) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + 10\text{H}_2\text{O}(g)$ | $K_P = 4.08 \times 10^{-25}$ at $25^\circ\text{C}$ |
| (d) $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  | $K_P = 0.122$ at $50^\circ\text{C}$                |
- 

**Solution:**

- (a)  $K_P = 1.6 \times 10^{-4}$ ; (b)  $K_P = 50.2$ ; (c)  $K_c = 5.34 \times 10^{-39}$ ; (d)  $K_c = 4.60 \times 10^{-3}$

**Exercise:**

**Problem:** Convert the values of  $K_c$  to values of  $K_P$  or the values of  $K_P$  to values of  $K_c$ .

- |   |  |
|---|--|
| (a) $\text{Cl}_2(g) + \text{Br}_2(g) \rightleftharpoons 2\text{BrCl}(g)$                                      | $K_c = 4.7 \times 10^{-2}$ at $25^\circ\text{C}$   |
| (b) $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$                                      | $K_P = 48.2$ at $500^\circ\text{C}$                |
| (c) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(s) \rightleftharpoons \text{CaCl}_2(s) + 6\text{H}_2\text{O}(g)$ | $K_P = 5.09 \times 10^{-44}$ at $25^\circ\text{C}$ |
| (d) $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  | $K_P = 0.196$ at $60^\circ\text{C}$                |

**Exercise:****Problem:**

What is the value of the equilibrium constant expression for the change  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  at  $30^\circ\text{C}$ ? (See [Appendix E](#).)

---

**Solution:**

$$K_P = P_{\text{H}_2\text{O}} = 0.042.$$

**Exercise:**

**Problem:** Write the expression of the reaction quotient for the ionization of HOCN in water.

**Exercise:**

**Problem:** Write the reaction quotient expression for the ionization of  $\text{NH}_3$  in water.

---

**Solution:**

$$Q_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

**Exercise:****Problem:**

What is the approximate value of the equilibrium constant  $K_P$  for the change  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(l) \rightleftharpoons \text{C}_2\text{H}_5\text{OC}_2\text{H}_5(g)$  at  $25^\circ\text{C}$ . (The equilibrium vapor pressure for this substance is 570 torr at  $25^\circ\text{C}$ .)

## Glossary

equilibrium constant ( $K$ )

value of the reaction quotient for a system at equilibrium; may be expressed using concentrations ( $K_c$ ) or partial pressures ( $K_p$ )

heterogeneous equilibria

equilibria in which reactants and products occupy two or more different phases

homogeneous equilibria

equilibria in which all reactants and products occupy the same phase

law of mass action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient ( $Q$ )

mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations ( $Q_c$ ) or pressures ( $Q_p$ )

## Shifting Equilibria: Le Châtelier's Principle

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by **Le Châtelier's principle**: *if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.*

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

### Effect of a Change in Concentration

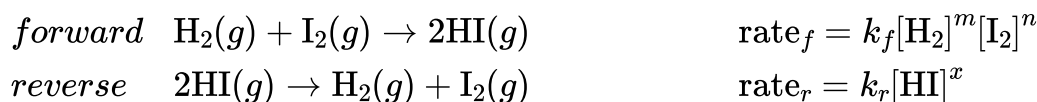
If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

**Equation:**



The rate laws for the forward and reverse reactions are

**Equation:**



When this system is at equilibrium, the forward and reverse reaction rates are equal.

**Equation:**

$$\text{rate}_f = \text{rate}_r$$

If the system is stressed by adding reactant, either  $\text{H}_2$  or  $\text{I}_2$ , the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

**Equation:**

$$\text{rate}_f > \text{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (*the equilibrium will shift right*). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

**Equation:**

$$\text{rate}_f < \text{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

**Equation:**

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then  $Q_c < K_c$  and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If  $\text{H}_2$  is added, the right shift will consume  $\text{I}_2$  and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of  $\text{H}_2$  and HI and a lesser concentration of  $\text{I}_2$  than was present before. If  $\text{I}_2$  is added, the new equilibrium mixture will have greater concentrations of  $\text{I}_2$  and HI and a lesser concentration of  $\text{H}_2$ . Finally, if HI is removed, the new equilibrium mixture will have greater concentrations of  $\text{H}_2$  and  $\text{I}_2$  and a lesser concentration of HI. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic

may be applied for stresses involving removing reactants or adding product, in which case  $Q_c > K_c$  and the equilibrium will shift left.

For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure  $P$  of an ideal gas is proportional to its molar concentration  $M$ ,

**Equation:**

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  is described by the reaction quotient

**Equation:**

$$Q_p = \frac{P_{\text{HI}^2}}{P_{\text{H}^2} P_{\text{I}^2}} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

**Equation:**

$$Q_p' = \frac{(3P_{\text{HI}^2})^2}{3P_{\text{H}^2} 3P_{\text{I}^2}} = \frac{9P_{\text{HI}^2}}{9P_{\text{H}^2} P_{\text{I}^2}} = \frac{P_{\text{HI}^2}}{P_{\text{H}^2} P_{\text{I}^2}} = Q_p = K_p$$
$$Q_p' = Q_p = K_p$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system,  $2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g)$ , however, yields a different result:

**Equation:**



$$Q_p = \frac{P_{\text{NO}_2} P_{\text{O}_2}}{P_{(\text{NO}_2)^2}} = K_p$$

$$Q_p' = \frac{(3P_{\text{NO}})^2 3P_{\text{O}_2}}{(3P_{\text{NO}_2})^2} = \frac{9P_{\text{NO}_2} 3P_{\text{O}_2}}{9P_{(\text{NO}_2)^2}} = \frac{27P_{\text{NO}_2} P_{\text{O}_2}}{P_{(\text{NO}_2)^2}} = 3Q_p > K_p$$

$$Q_p' = 3Q_p > K_p$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better “accommodates” the volume change. In the second example, two moles of reactant ( $\text{NO}_2$ ) yield three moles of product ( $2\text{NO} + \text{O}_2$ ), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

**Note:**

Check out this [link](#) to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

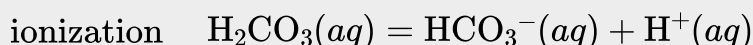
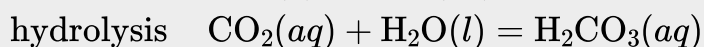
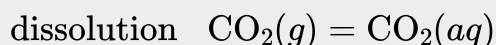
**Note:**

**Equilibrium and Soft Drinks**

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestley’s approach involved production of carbon dioxide by reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

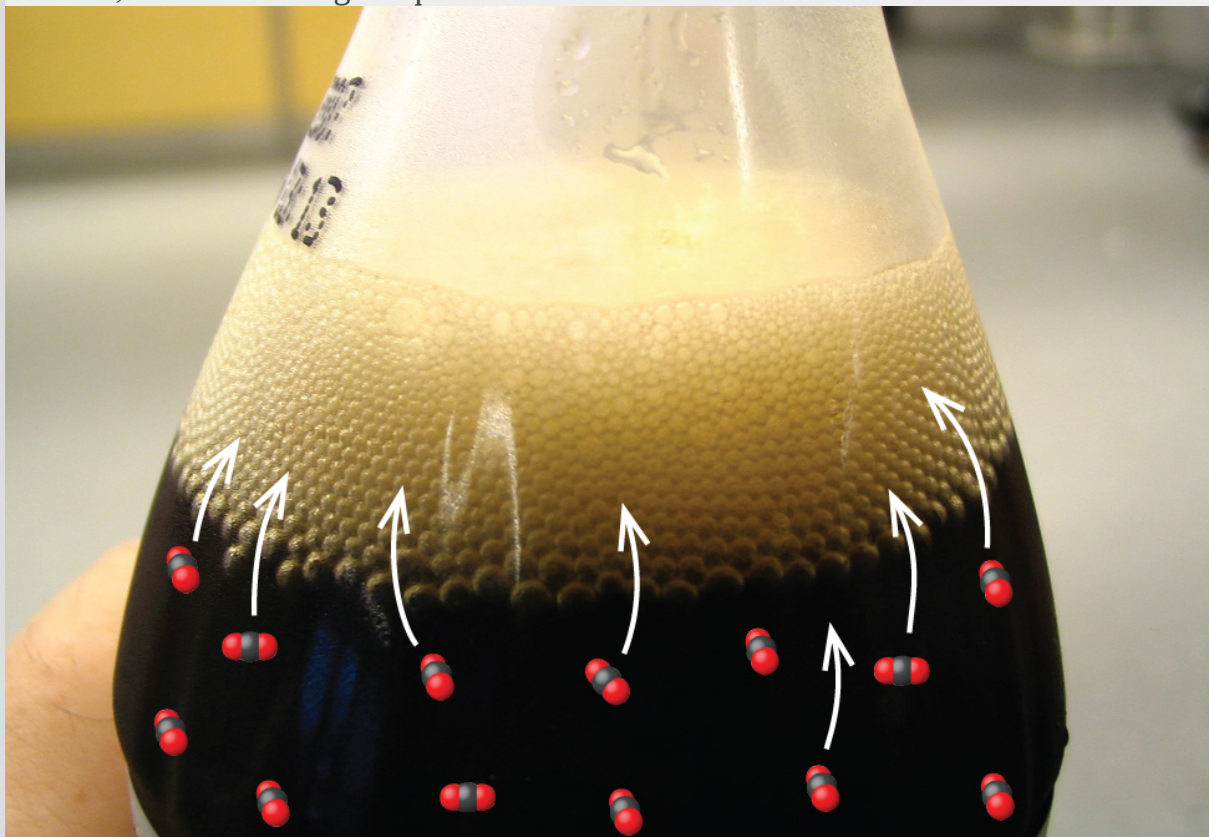
The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

**Equation:**



These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

When a carbonated beverage container is opened, a hissing sound is heard as pressurized  $\text{CO}_2$  escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved  $\text{CO}_2$  and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the  $\text{CO}_2(\text{aq})$  concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."



Opening a soft-drink bottle lowers the  $\text{CO}_2$  pressure above the beverage, shifting

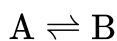
the dissolution equilibrium and releasing dissolved CO<sub>2</sub> from the beverage.  
(credit: modification of work by “D Coetzee”/Flickr)

## Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant,  $K$ . When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

**Equation:**



Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

**Equation:**

$$\text{rate}_f = k_f[A]$$

$$\text{rate}_r = k_r[B]$$

When the system is at equilibrium,

**Equation:**

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

**Equation:**

$$k_f[A] = k_r[B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as

described by the Arrhenius equation, it stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

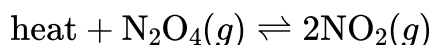
Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

**Equation:**



For purposes of applying Le Chatelier's principle, heat ( $q$ ) may be viewed as a reactant:

**Equation:**



Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

**Note:**

This interactive [animation](#) allows you to apply Le Châtelier's principle to predict the effects of changes in concentration, pressure, and temperature on reactant and product concentrations.

## Key Concepts and Summary

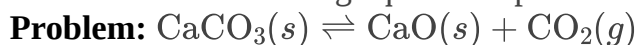
Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Châtelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible

process, increasing the rate at which equilibrium is reached but not altering the equilibrium mixture's composition ( $K$  does not change).

## Chemistry End of Chapter Exercises

### Exercise:

The following equation represents a reversible decomposition:



Under what conditions will decomposition in a closed container proceed to completion so that no  $\text{CaCO}_3$  remains?

---

### Solution:

The amount of  $\text{CaCO}_3$  must be so small that  $P_{\text{CO}_2}$  is less than  $K_P$  when the  $\text{CaCO}_3$  has completely decomposed. In other words, the starting amount of  $\text{CaCO}_3$  cannot completely generate the full  $P_{\text{CO}_2}$  required for equilibrium.

### Exercise:

#### Problem:

Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

### Exercise:

#### Problem:

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

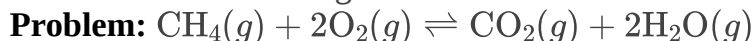
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### Solution:

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

### Exercise:

The following reaction occurs when a burner on a gas stove is lit:



Is an equilibrium among  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  established under these conditions? Explain your answer.

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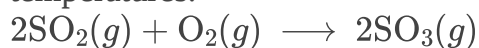
**Solution:**

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

**Exercise:**

**Problem:**

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide,  $\text{SO}_3$ , from sulfur dioxide,  $\text{SO}_2$ , and oxygen,  $\text{O}_2$ , shown here. At high temperatures, the rate of formation of  $\text{SO}_3$  is higher, but the equilibrium amount (concentration or partial pressure) of  $\text{SO}_3$  is lower than it would be at lower temperatures.



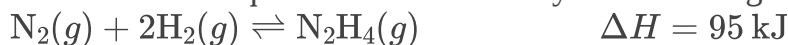
(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

**Exercise:**

**Problem:**

Suggest four ways in which the concentration of hydrazine,  $\text{N}_2\text{H}_4$ , could be increased in an equilibrium described by the following equation:



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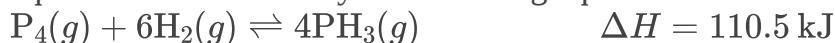
**Solution:**

Add  $\text{N}_2$ ; add  $\text{H}_2$ ; decrease the container volume; heat the mixture.

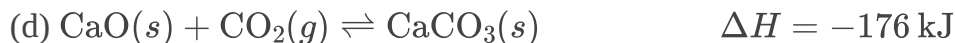
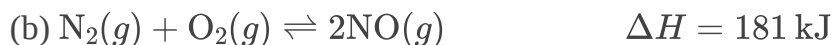
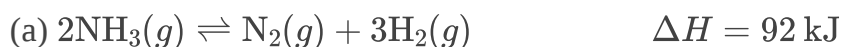
**Exercise:**

**Problem:**

Suggest four ways in which the concentration of  $\text{PH}_3$  could be increased in an equilibrium described by the following equation:

**Exercise:****Problem:**

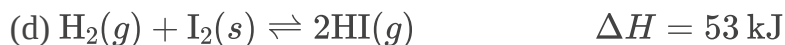
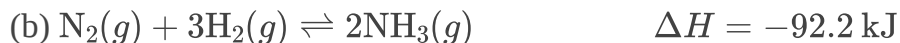
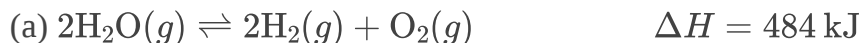
How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

**Solution:**

(a)  $T$  increase = shift right,  $V$  decrease = shift left; (b)  $T$  increase = shift right,  $V$  = no effect; (c)  $T$  increase = shift left,  $V$  decrease = shift left; (d)  $T$  increase = shift left,  $V$  decrease = shift right.

**Exercise:****Problem:**

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

**Exercise:**

**Problem:**

Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant ( $K_c$ ) for the reversible reaction  
 $2\text{H}_2(g) + \text{CO}(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \quad \Delta H = -90.2 \text{ kJ}$

(b) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more  $\text{H}_2$  is added?

(c) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CO}$  is removed?

(d) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CH}_3\text{OH}$  is added?

(e) What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if the temperature of the system is increased?

---

**Solution:**

(a)  $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2[\text{CO}]}$ ; (b)  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  increases; (c),  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  decreases; (d),  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  increases; (e),  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  decreases

**Exercise:**

**Problem:** Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant ( $K_c$ ) for the reversible reaction  
 $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H = 181 \text{ kJ}$

(b) What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if more  $\text{O}_2$  is added?

(c) What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if  $\text{N}_2$  is removed?

(d) What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if  $\text{NO}$  is added?



(e) What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if the temperature of the system is increased?

**Exercise:**

**Problem:**

Water gas, a mixture of  $\text{H}_2$  and  $\text{CO}$ , is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction  
 $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g) \quad \Delta H = 131.30 \text{ kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more  $\text{C}$  is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if  $\text{CO}$  is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

---

**Solution:**

(a)  $K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$ ; (b)  $[\text{H}_2\text{O}]$  no change,  $[\text{CO}]$  no change,  $[\text{H}_2]$  no change; (c)  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  decreases,  $[\text{H}_2]$  decreases; (d)  $[\text{H}_2\text{O}]$  increases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  decreases; (f)  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

**Exercise:**

**Problem:**

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant ( $K_c$ ) for the reversible reaction  
 $\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightleftharpoons 2\text{Fe}(s) + 3\text{H}_2\text{O}(g) \quad \Delta H = 98.7 \text{ kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2$  is added?

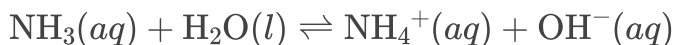
(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

**Exercise:**

**Problem:**

Ammonia is a weak base that reacts with water according to this equation:



Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of  $\text{NH}_4\text{Cl}$

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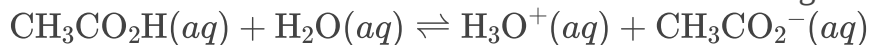
**Solution:**

Only (b)

**Exercise:**

**Problem:**

Acetic acid is a weak acid that reacts with water according to this equation:



Will any of the following increase the percent of acetic acid that reacts and produces  $\text{CH}_3\text{CO}_2^-$  ion?

(a) Addition of HCl

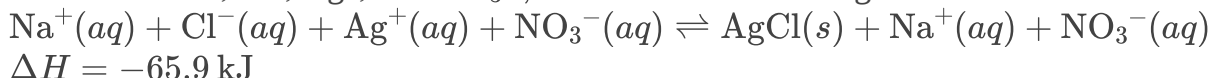
(b) Addition of NaOH

(c) Addition of NaCH<sub>3</sub>CO<sub>2</sub>

**Exercise:**

**Problem:**

Suggest two ways in which the equilibrium concentration of Ag<sup>+</sup> can be reduced in a solution of Na<sup>+</sup>, Cl<sup>-</sup>, Ag<sup>+</sup>, and NO<sub>3</sub><sup>-</sup>, in contact with solid AgCl.



**Solution:**

Add NaCl or some other salt that produces Cl<sup>-</sup> to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

**Exercise:**

**Problem:**

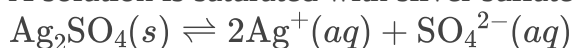
How can the pressure of water vapor be increased in the following equilibrium?



**Exercise:**

**Problem:**

A solution is saturated with silver sulfate and contains excess solid silver sulfate:



A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag<sup>+</sup> ions. Explain this observation.

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**Solution:**

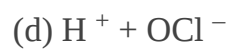
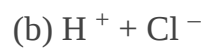
(a)

**Exercise:**

**Problem:**

When equal molar amounts of HCl and HOCl are dissolved separately in equal amounts of water, the solution of HCl freezes at a lower temperature. Which compound has the larger equilibrium constant for acid ionization?

(a) HCl



## **Glossary**

Le Châtelier's principle

an equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium

## Equilibrium Calculations

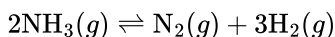
By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

**Equation:**



As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either  $\text{NH}_3$  only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount  $x$ :

**Equation:**

$$\Delta [\text{N}_2] = +x,$$

the corresponding changes in the other species concentrations are

**Equation:**

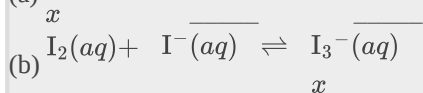
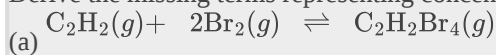
$$\begin{aligned}\Delta[\text{H}_2] &= \Delta[\text{N}_2] \left( \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} \right) = +3x \\ \Delta[\text{NH}_3] &= -\Delta[\text{N}_2] \left( \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} \right) = -2x,\end{aligned}$$

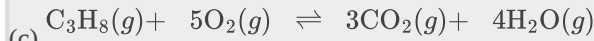
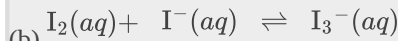
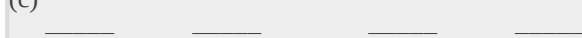
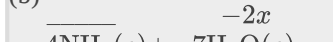
where the negative sign indicates a decrease in concentration.

### Example:

#### Determining Relative Changes in Concentration

Derive the missing terms representing concentration changes for each of the following reactions.




$$(a) \quad 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$$


(a)  $2x, x, -2x$ ; (b)  $x, -2x$ ; (c)  $4x, 7x, -4x, -6x$  or  $-4x, -7x, 4x, 6x$

**Equation:**

$$K_C = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	$\text{I}_2$	+	$\text{I}^-$	$\rightleftharpoons$	$\text{I}_3^-$
<b>Initial concentration (M)</b>	$1.000 \times 10^{-3}$		$1.000 \times 10^{-3}$		0
<b>Change (M)</b>	$-x$		$-x$		$+x$
<b>Equilibrium concentration (M)</b>	$1.000 \times 10^{-3} - x$		$1.000 \times 10^{-3} - x$		$x$

At equilibrium the concentration of  $\text{I}_2$  is  $6.61 \times 10^{-4} \text{ M}$  so that

**Equation:**

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

**Equation:**

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

**Equation:**

$$= 3.39 \times 10^{-4} \text{ M}$$

The ICE table may now be updated with numerical values for all its concentrations:

	$\text{I}_2$	+	$\text{I}^-$	$\rightleftharpoons$	$\text{I}_3^-$
<b>Initial concentration (M)</b>	$1.000 \times 10^{-3}$		$1.000 \times 10^{-3}$		0
<b>Change (M)</b>	$-3.39 \times 10^{-4}$		$-3.39 \times 10^{-4}$		$+3.39 \times 10^{-4}$
<b>Equilibrium concentration (M)</b>	$6.61 \times 10^{-4}$		$6.61 \times 10^{-4}$		$3.39 \times 10^{-4}$

Finally, substitute the equilibrium concentrations into the  $K$  expression and solve:

**Equation:**

$$K_c = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$$

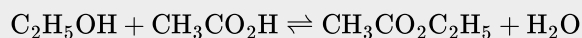
**Equation:**

$$= \frac{3.39 \times 10^{-4} \text{ M}}{(6.61 \times 10^{-4} \text{ M})(6.61 \times 10^{-4} \text{ M})} = 776$$

**Check Your Learning**

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

**Equation:**



When 1 mol each of  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{CO}_2\text{H}$  are allowed to react in 1 L of the solvent dioxane, equilibrium is established when  $\frac{1}{3}$  mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is a solute in this reaction.)

**Note:**

**Answer:**

$$K_c = 4$$

**Calculation of a Missing Equilibrium Concentration**

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

**Example:****Calculation of a Missing Equilibrium Concentration**

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the  $K_c$  for the reaction,  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ , is  $4.1 \times 10^{-4}$ . Calculate the equilibrium concentration of  $\text{NO}(g)$  in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of  $\text{N}_2$  and  $\text{O}_2$  at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

**Solution**

Substitute the provided quantities into the equilibrium constant expression and solve for  $[\text{NO}]$ :

**Equation:**

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2] [\text{O}_2]}$$

**Equation:**

$$[\text{NO}]^2 = K_c [\text{N}_2] [\text{O}_2]$$

**Equation:**

$$[\text{NO}] = \sqrt{K_c [\text{N}_2] [\text{O}_2]}$$

**Equation:**

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

**Equation:**



$$= \sqrt{1.31 \times 10^{-7}}$$

**Equation:**

$$= 3.6 \times 10^{-4}$$

Thus  $[\text{NO}]$  is  $3.6 \times 10^{-4} \text{ mol/L}$  at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for  $K$ :

**Equation:**

$$\begin{aligned} K_c &= \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \\ &= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)} \\ &= 4.0 \times 10^{-4} \end{aligned}$$

This result is consistent with the provided value for  $K$  within nominal uncertainty, differing by just 1 in the least significant digit's place.

### Check Your Learning

The equilibrium constant  $K_c$  for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is  $6.00 \times 10^{-2}$ . Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are  $4.26 \text{ M}$  and  $2.09 \text{ M}$ , respectively.

**Note:**

**Answer:**

$1.53 \text{ mol/L}$

## Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Develop an ICE table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

**Example:**

### Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant  $K_c$  for the decomposition of  $\text{PCl}_5(g)$  into  $\text{PCl}_3(g)$  and  $\text{Cl}_2(g)$  is 0.0211. What are the equilibrium concentrations of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  in a mixture that initially contained only  $\text{PCl}_5$  at a concentration of  $1.00 \text{ M}$ ?

**Solution**

Use the stepwise process described earlier.

Determine the direction the reaction proceeds.

The balanced equation for the decomposition of  $\text{PCl}_5$  is

Equation:



Because only the reactant is present initially  $Q_c = 0$  and the reaction will proceed to the right.

Develop an ICE table.

	$\text{PCl}_5$	$\rightleftharpoons$	$\text{PCl}_3$	+	$\text{Cl}_2$
Initial concentration (M)	1.00		0		0
Change (M)	$-x$		$+x$		$+x$
Equilibrium concentration (M)	$1.00 - x$		$x$		$x$

Solve for the change and the equilibrium concentrations.

Substituting the equilibrium concentrations into the equilibrium constant equation gives

Equation:

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 0.0211$$

Equation:

$$= \frac{(x)(x)}{(1.00 - x)} 0.0211$$

Equation:

$$= \frac{(x)(x)}{(1.00 - x)} 0.0211(1.00 -$$

Equation:

$$0.0211(1.00 -$$

Confirm the calculated equilibrium concentrations.

Substitution into the expression for  $K_c$  (to check the calculation) gives

Equation:

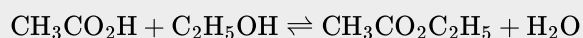
$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of  $K_c$  given in the problem (when rounded to the proper number of significant figures).

### Check Your Learning

Acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , reacts with ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , to form water and ethyl acetate,  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ .

Equation:



The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations for a mixture that is initially 0.15 M in  $\text{CH}_3\text{CO}_2\text{H}$ , 0.15 M in  $\text{C}_2\text{H}_5\text{OH}$ , 0.40 M in  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ , and 0.40 M in  $\text{H}_2\text{O}$ ?

Note:

Answer:

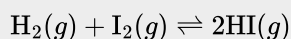
$[\text{CH}_3\text{CO}_2\text{H}] = 0.37 \text{ M}$ ,  $[\text{C}_2\text{H}_5\text{OH}] = 0.37 \text{ M}$ ,  $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.18 \text{ M}$ ,  $[\text{H}_2\text{O}] = 0.18 \text{ M}$

### Check Your Learning

A 1.00-L flask is filled with 1.00 moles of  $\text{H}_2$  and 2.00 moles of  $\text{I}_2$ . The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the

equilibrium concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  in moles/L?

**Equation:**



**Note:**

**Answer:**

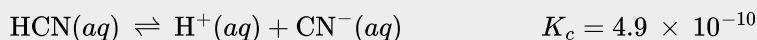
$[\text{H}_2] = 0.06\text{ M}$ ,  $[\text{I}_2] = 1.06\text{ M}$ ,  $[\text{HI}] = 1.88\text{ M}$

**Example:**

**Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption**

What are the concentrations at equilibrium of a  $0.15\text{ M}$  solution of  $\text{HCN}$ ?

**Equation:**



**Solution**

Using “ $x$ ” to represent the concentration of each product at equilibrium gives this ICE table.

	$\text{HCN}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CN}^-(aq)$		
Initial concentration ( $M$ )	0.15	0	0
Change ( $M$ )	$-x$	$+x$	$+x$
Equilibrium concentration ( $M$ )	$0.15 - x$	$x$	$x$

Substitute the equilibrium concentration terms into the  $K_c$  expression

**Equation:**

$$K_c = \frac{(x)(x)}{0.15 - x}$$

Rearrange to the quadratic form and solve for  $x$

**Equation:**

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

**Equation:**

$$x = 8.56 \times 10^{-6}\text{ M (3 sig. figs.)} = 8.6 \times 10^{-6}\text{ M (2 sig. figs.)}$$

Thus  $[\text{H}^+] = [\text{CN}^-] = x = 8.6 \times 10^{-6}\text{ M}$  and  $[\text{HCN}] = 0.15 - x = 0.15\text{ M}$ .

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small  $K$ ), and so the initial concentration experiences a negligible change:

**Equation:**

if  $x \ll 0.15 \text{ M}$ , then  $(0.15 - x) \approx 0.15$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

**Equation:**

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

**Equation:**

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

**Equation:**

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

**Equation:**

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6} \text{ M}$$

The value of  $x$  calculated is, indeed, much less than the initial concentration

**Equation:**

$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for  $x$  that did *not* justify the approximation, the calculation would need to be repeated without making the approximation.

#### Check Your Learning

What are the equilibrium concentrations in a  $0.25 \text{ M NH}_3$  solution?

**Equation:**



**Note:**

**Answer:**

$$[\text{OH}^-] = [\text{NH}_4^+] = 0.0021 \text{ M}; [\text{NH}_3] = 0.25 \text{ M}$$

## Temperature Dependence of Spontaneity

As was previously demonstrated in the section on entropy in an earlier chapter, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

**Equation:**

$$\Delta G = \Delta H - T\Delta S$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since  $T$  is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both  $\Delta H$  and  $\Delta S$  are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case,  $\Delta G$  will be negative if the magnitude of the  $T\Delta S$  term is greater than  $\Delta H$ . If the  $T\Delta S$  term is less than  $\Delta H$ , the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures*.
2. **Both  $\Delta H$  and  $\Delta S$  are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case,  $\Delta G$  will be negative if the magnitude of the  $T\Delta S$  term is less than  $\Delta H$ . If the  $T\Delta S$  term's magnitude is greater than  $\Delta H$ , the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures*.
3.  **$\Delta H$  is positive and  $\Delta S$  is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case,  $\Delta G$  will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures*.
4.  **$\Delta H$  is negative and  $\Delta S$  is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case,  $\Delta G$  will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures*.

These four scenarios are summarized in [\[link\]](#).

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature  Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

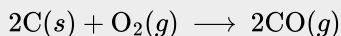
There are four possibilities regarding the signs of enthalpy and entropy changes.

#### Example:

##### Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

##### Equation:



How does the spontaneity of this process depend upon temperature?

##### Solution

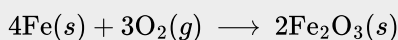
Combustion processes are exothermic ( $\Delta H < 0$ ). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas,  $\Delta S > 0$ ). The reaction is

therefore spontaneous ( $\Delta G < 0$ ) at all temperatures.

**Check Your Learning**

Popular chemical hand warmers generate heat by the air-oxidation of iron:

**Equation:**



How does the spontaneity of this process depend upon temperature?

**Note:**

**Answer:**

$\Delta H$  and  $\Delta S$  are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its  $\Delta G$ ) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which  $\Delta G$  is plotted on the y axis versus  $T$  on the x axis:

**Equation:**

$$\Delta G = \Delta H - T\Delta S$$

**Equation:**

$$y = b + mx$$

Such a plot is shown in [\[link\]](#). A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative  $\Delta G$ ) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of  $T$  for which  $\Delta G$  is zero:

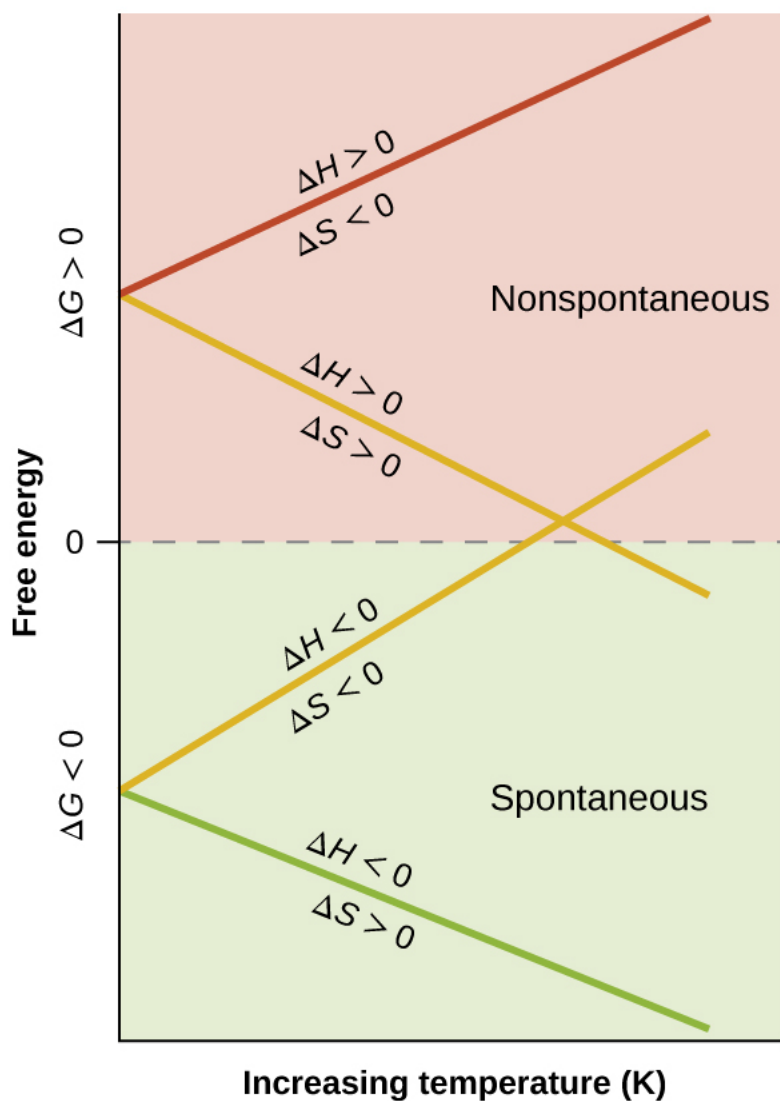
**Equation:**

$$\Delta G = 0 = \Delta H - T\Delta S$$

**Equation:**

$$T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which  $\Delta G$  for the process is zero. As noted earlier, the condition of  $\Delta G = 0$  describes a system at equilibrium.



These plots show the variation in  $\Delta G$  with temperature for the four possible combinations of arithmetic sign for  $\Delta H$  and  $\Delta S$ .

**Example:**

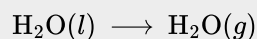
**Equilibrium Temperature for a Phase Transition**

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in [Appendix G](#) to estimate the boiling point of water.

**Solution**

The process of interest is the following phase change:

**Equation:**



When this process is at equilibrium,  $\Delta G = 0$ , so the following is true:

**Equation:**

$$0 = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from [Appendix G](#),

**Equation:**

$$\begin{aligned}\Delta H^\circ &= 1 \text{ mol} \times \Delta H_f^\circ(\text{H}_2\text{O}(g)) - 1 \text{ mol} \times \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= (1 \text{ mol}) - 241.82 \text{ kJ/mol} - (1 \text{ mol})(-241.82 \text{ kJ/mol}) = 44.01 \text{ kJ} \\ \Delta S^\circ &= 1 \text{ mol} \times \Delta S^\circ(\text{H}_2\text{O}(g)) - 1 \text{ mol} \times \Delta S^\circ(\text{H}_2\text{O}(l)) \\ &= (1 \text{ mol})188.8 \text{ J/K}\cdot\text{mol} - (1 \text{ mol})70.0 \text{ J/K}\cdot\text{mol} = 118.8 \text{ J/K} \\ T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3 \text{ J}}{118.8 \text{ J/K}} = 370.5 \text{ K} = 97.3^\circ \text{C}\end{aligned}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K ([Appendix G](#)). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

**Check Your Learning**

Use the information in [Appendix G](#) to estimate the boiling point of CS<sub>2</sub>.

**Note:**

**Answer:**

313 K (accepted value 319 K)

## Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for  $\Delta G$  represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When  $\Delta G$  is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium).

In the section on equilibrium, the *reaction quotient*,  $Q$ , was introduced as a convenient measure of the status of an equilibrium system. Recall that  $Q$  is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When  $Q$  is lesser than the equilibrium constant,  $K$ , the reaction will proceed in the forward direction until equilibrium is reached and  $Q = K$ . Conversely, if  $Q > K$ , the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change, according to this equation:

**Equation:**

$$\Delta G = \Delta G^\circ + RT \ln Q$$



$R$  is the gas constant (8.314 J/K mol),  $T$  is the kelvin or absolute temperature, and  $Q$  is the reaction quotient. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in [\[link\]](#).

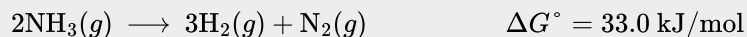
**Example:**

**Calculating  $\Delta G$  under Nonstandard Conditions**

What is the free energy change for the process shown here under the specified conditions?

$T = 25\text{ }^{\circ}\text{C}$ ,  $P_{\text{N}_2} = 0.870\text{ atm}$ ,  $P_{\text{H}_2} = 0.250\text{ atm}$ , and  $P_{\text{NH}_3} = 12.9\text{ atm}$

**Equation:**



**Solution**

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

**Equation:**

$$\Delta G = \Delta G^{\circ} + RT \ln Q = 33.0 \frac{\text{kJ}}{\text{mol}} + \left( 8.314 \frac{\text{J}}{\text{mol K}} \times 298\text{ K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2} \right) = 9680 \frac{\text{J}}{\text{mol}}$$

Since the computed value for  $\Delta G$  is positive, the reaction is nonspontaneous under these conditions.

**Check Your Learning**

Calculate the free energy change for this same reaction at  $875\text{ }^{\circ}\text{C}$  in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

**Note:**

**Answer:**

$\Delta G = -47\text{ kJ/mol}$ ; yes

For a system at equilibrium,  $Q = K$  and  $\Delta G = 0$ , and the previous equation may be written as

**Equation:**

$$0 = \Delta G^{\circ} + RT \ln K \qquad (\text{at equilibrium})$$

**Equation:**

$$\Delta G^{\circ} = -RT \ln K \qquad \text{or} \qquad K = e^{-\frac{\Delta G^{\circ}}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in [\[link\]](#).

### Relations between Standard Free Energy Changes and Equilibrium Constants

$K$	$\Delta G^\circ$	Composition of an Equilibrium Mixture
$> 1$	$< 0$	Products are more abundant
$< 1$	$> 0$	Reactants are more abundant
$= 1$	$= 0$	Reactants and products are comparably abundant

#### Example:

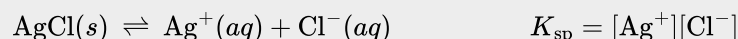
##### Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of  $\text{Ag}^+(aq)$ ,  $\text{Cl}^-(aq)$ , and  $\text{AgCl}(s)$  are 77.1 kJ/mol, -131.2 kJ/mol, and -109.8 kJ/mol, respectively, calculate the solubility product,  $K_{\text{sp}}$ , for  $\text{AgCl}$ .

##### Solution

The reaction of interest is the following:

##### Equation:



The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

##### Equation:

$$\begin{aligned} \Delta G^\circ &= [\Delta G_f^\circ(\text{Ag}^+(aq)) + \Delta G_f^\circ(\text{Cl}^-(aq))] - [\Delta G_f^\circ(\text{AgCl}(s))] \\ &= [77.1 \text{ kJ/mol} - 131.2 \text{ kJ/mol}] - [-109.8 \text{ kJ/mol}] = 55.7 \text{ kJ/mol} \end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

##### Equation:

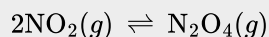
$$K_{\text{sp}} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K} \times 298.15 \text{ K}}\right) = \exp(-22.470) = e^{-22.470} = 1.$$

This result is in reasonable agreement with the value provided in [Appendix J](#).

#### Check Your Learning

Use the thermodynamic data provided in [Appendix G](#) to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

##### Equation:

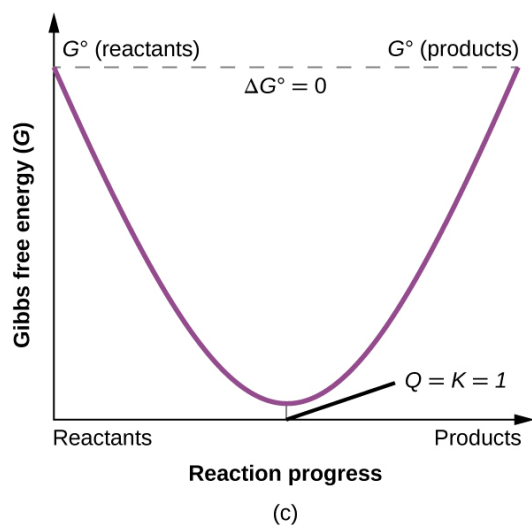
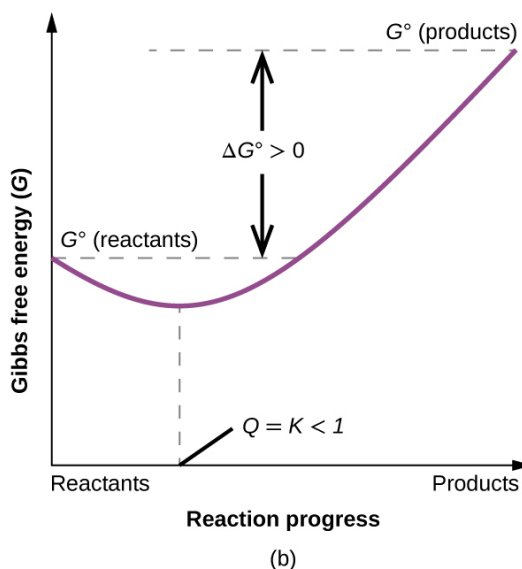
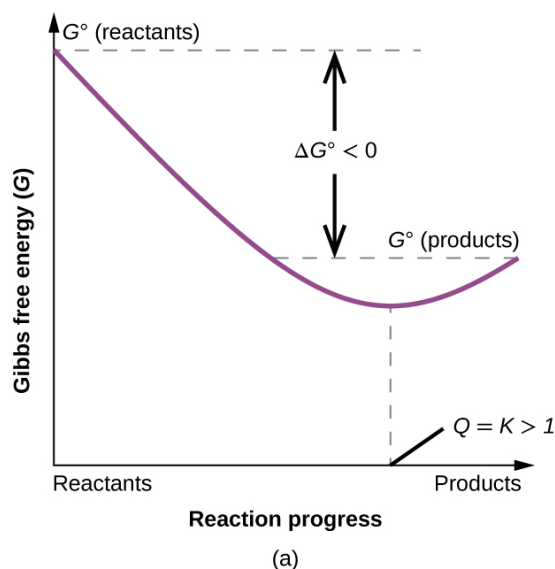


##### Note:

##### Answer:

$$K = 6.9$$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of  $Q$ ), equilibrium is established when the system's free energy is minimized ([link](#)). If a system consists of reactants and products in nonequilibrium amounts ( $Q \neq K$ ), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.



These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

## Key Concepts and Summary

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for several types of equilibrium calculations. We also learned that a negative value for  $\Delta G$  indicates a spontaneous process; a positive  $\Delta G$  indicates a nonspontaneous process; and a  $\Delta G$  of zero indicates that the system is at equilibrium. We also saw how free energy, spontaneity, and equilibrium relate.

## Key Equations

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -RT \ln K$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

A reaction is represented by this equation:  $A(aq) + 2B(aq) \rightleftharpoons 2C(aq)$   $K_c = 1 \times 10^3$

- Write the mathematical expression for the equilibrium constant.
- Using concentrations  $\leq 1 M$ , identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

#### Solution:

$$K_c = \frac{[C]^2}{[A][B]^2}. [A] = 0.1 M, [B] = 0.1 M, [C] = 1 M; \text{ and } [A] = 0.01, [B] = 0.250, [C] = 0.791.$$

### Exercise:

#### Problem:

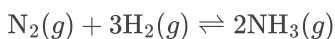
A reaction is represented by this equation:  $2W(aq) \rightleftharpoons X(aq) + 2Y(aq)$   $K_c = 5 \times 10^{-4}$

- Write the mathematical expression for the equilibrium constant.
- Using concentrations of  $\leq 1 M$ , identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

### Exercise:

#### Problem:

What is the value of the equilibrium constant at 500 °C for the formation of  $NH_3$  according to the following equation?



An equilibrium mixture of  $NH_3(g)$ ,  $H_2(g)$ , and  $N_2(g)$  at 500 °C was found to contain 1.35 M  $H_2$ , 1.15 M  $N_2$ , and  $4.12 \times 10^{-1} M NH_3$ .

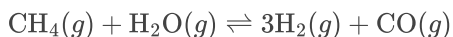
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**Solution:**

$$K_c = 6.00 \times 10^{-2}$$

**Exercise:****Problem:**

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.



What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations:  $\text{CH}_4$ , 0.126 M;  $\text{H}_2\text{O}$ , 0.242 M;  $\text{CO}$ , 0.126 M;  $\text{H}_2$  1.15 M, at a temperature of 760 °C?

**Exercise:****Problem:**

A 0.72-mol sample of  $\text{PCl}_5$  is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of  $\text{PCl}_3(g)$  and 0.40 mol of  $\text{Cl}_2(g)$ . Calculate the value of the equilibrium constant for the decomposition of  $\text{PCl}_5$  to  $\text{PCl}_3$  and  $\text{Cl}_2$  at this temperature.

---

**Solution:**

$$K_c = 0.50$$

**Exercise:****Problem:**

At 1 atm and 25 °C,  $\text{NO}_2$  with an initial concentration of 1.00 M is 0.0033% decomposed into NO and  $\text{O}_2$ . Calculate the value of the equilibrium constant for the reaction.

**Exercise:****Problem:**

Calculate the value of the equilibrium constant  $K_P$  for the reaction  $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$  from these equilibrium pressures: NO, 0.050 atm;  $\text{Cl}_2$ , 0.30 atm; NOCl, 1.2 atm.

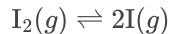
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**Solution:**

$$K_P = 1.9 \times 10^3$$

**Exercise:**

**Problem:** When heated, iodine vapor dissociates according to this equation:



At 1274 K, a sample exhibits a partial pressure of  $\text{I}_2$  of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant,  $K_P$ , for the decomposition at 1274 K.

**Exercise:**

**Problem:** A sample of ammonium chloride was heated in a closed container.



At equilibrium, the pressure of  $\text{NH}_3(g)$  was found to be 1.75 atm. What is the value of the equilibrium constant  $K_P$  for the decomposition at this temperature?

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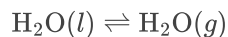
**Solution:**

$$K_P = 3.06$$

**Exercise:**

**Problem:**

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant  $K_P$  for the vaporization equilibrium at 60 °C?

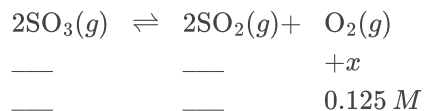


**Exercise:**

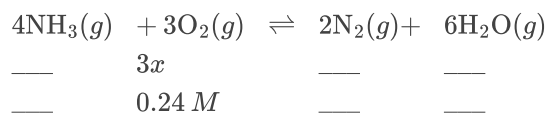
**Problem:**

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

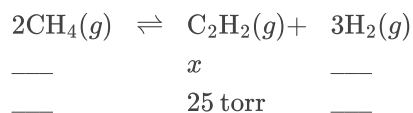
(a)



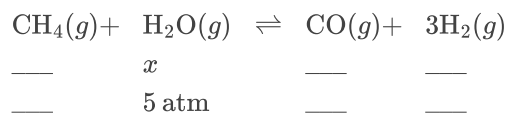
(b)



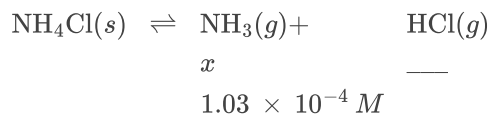
(c) Change in pressure:



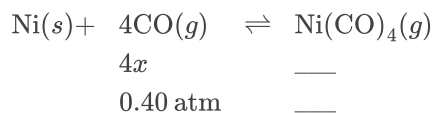
(d) Change in pressure:



(e)



(f) change in pressure:



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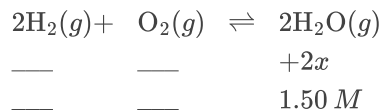
**Solution:**

(a)  $-2x$ ,  $2x$ ,  $-0.250\text{ M}$ ,  $0.250\text{ M}$ ; (b)  $4x$ ,  $-2x$ ,  $-6x$ ,  $0.32\text{ M}$ ,  $-0.16\text{ M}$ ,  $-0.48\text{ M}$ ; (c)  $-2x$ ,  $3x$ ,  $-50\text{ torr}$ ,  $75\text{ torr}$ ; (d)  $x$ ,  $-x$ ,  $-3x$ ,  $5\text{ atm}$ ,  $-5\text{ atm}$ ,  $-15\text{ atm}$ ; (e)  $x$ ,  $1.03 \times 10^{-4}\text{ M}$ ; (f)  $x$ ,  $0.1\text{ atm}$ .

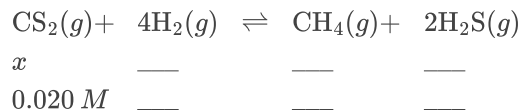
**Exercise:****Problem:**

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

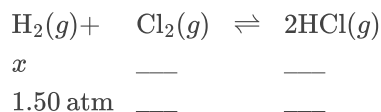
(a)



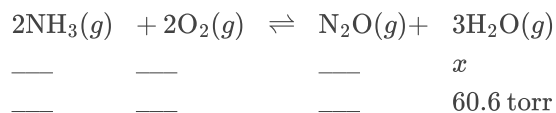
(b)



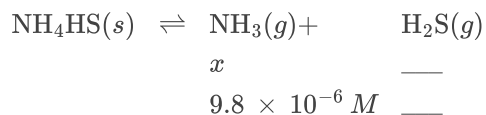
(c) Change in pressure:



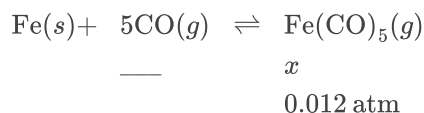
(d) Change in pressure:



(e)



(f) Change in pressure:

**Exercise:**

**Problem:** Why are there no changes specified for Ni in [\[link\]](#), part (f)? What property of Ni does change?

---

**Solution:**

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

**Exercise:**

**Problem:**

Why are there no changes specified for  $\text{NH}_4\text{HS}$  in [\[link\]](#), part (e)? What property of  $\text{NH}_4\text{HS}$  does change?

**Exercise:****Problem:**

Analysis of the gases in a sealed reaction vessel containing  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  at equilibrium at  $400^\circ\text{C}$  established the concentration of  $\text{N}_2$  to be  $1.2\text{ M}$  and the concentration of  $\text{H}_2$  to be  $0.24\text{ M}$ .



Calculate the equilibrium molar concentration of  $\text{NH}_3$ .

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**Solution:**

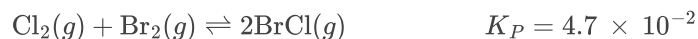
$$[\text{NH}_3] = 9.1 \times 10^{-2}\text{ M}$$

**Exercise:****Problem:**

Calculate the number of moles of  $\text{HI}$  that are at equilibrium with  $1.25\text{ mol}$  of  $\text{H}_2$  and  $1.25\text{ mol}$  of  $\text{I}_2$  in a  $5.00\text{-L}$  flask at  $448^\circ\text{C}$ .

**Exercise:****Problem:**

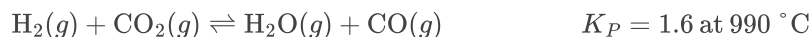
What is the pressure of  $\text{BrCl}$  in an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{BrCl}$  if the pressure of  $\text{Cl}_2$  in the mixture is  $0.115\text{ atm}$  and the pressure of  $\text{Br}_2$  in the mixture is  $0.450\text{ atm}$ ?

**Solution:**

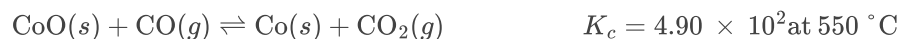
$$P_{\text{BrCl}} = 4.9 \times 10^{-2}\text{ atm}$$

**Exercise:****Problem:**

What is the pressure of  $\text{CO}_2$  in a mixture at equilibrium that contains  $0.50\text{ atm}$   $\text{H}_2$ ,  $2.0\text{ atm}$  of  $\text{H}_2\text{O}$ , and  $1.0\text{ atm}$  of  $\text{CO}$  at  $990^\circ\text{C}$ ?

**Exercise:**

**Problem:** Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.



What concentration of  $\text{CO}$  remains in an equilibrium mixture with  $[\text{CO}_2] = 0.100\text{ M}$ ?

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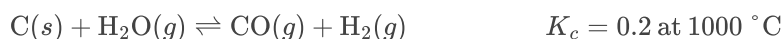
**Solution:**

$$[\text{CO}] = 2.04 \times 10^{-4}\text{ M}$$



**Exercise:**

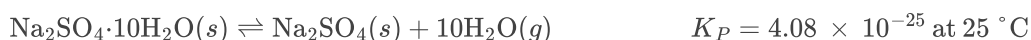
**Problem:** Carbon reacts with water vapor at elevated temperatures.



Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with  $[\text{H}_2\text{O}] = 0.500 \text{ M}$  at  $1000^\circ\text{C}$ ?

**Exercise:**

**Problem:** Sodium sulfate 10-hydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , dehydrates according to the equation



What is the pressure of water vapor at equilibrium with a mixture of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$ ?

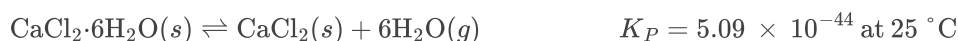
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**Solution:**

$$P_{\text{H}_2\text{O}} = 3.64 \times 10^{-3} \text{ atm}$$

**Exercise:**

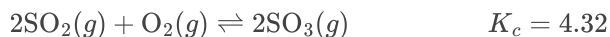
**Problem:** Calcium chloride 6-hydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , dehydrates according to the equation



What is the pressure of water vapor at equilibrium with a mixture of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2$  at  $25^\circ\text{C}$ ?

**Exercise:****Problem:**

A student solved the following problem and found the equilibrium concentrations to be  $[\text{SO}_2] = 0.590 \text{ M}$ ,  $[\text{O}_2] = 0.0450 \text{ M}$ , and  $[\text{SO}_3] = 0.260 \text{ M}$ . How could this student check the work without reworking the problem? The problem was: For the following reaction at  $600^\circ\text{C}$ :



What are the equilibrium concentrations of all species in a mixture that was prepared with  $[\text{SO}_3] = 0.500 \text{ M}$ ,  $[\text{SO}_2] = 0 \text{ M}$ , and  $[\text{O}_2] = 0.350 \text{ M}$ ?

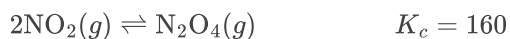
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**Solution:**

Calculate  $Q$  based on the calculated concentrations and see if it is equal to  $K_c$ . Because  $Q$  does equal 4.32, the system must be at equilibrium.

**Exercise:****Problem:**

A student solved the following problem and found  $[\text{N}_2\text{O}_4] = 0.16 \text{ M}$  at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of  $\text{N}_2\text{O}_4$  in a mixture formed from a sample of  $\text{NO}_2$  with a concentration of  $0.10 \text{ M}$ ?

**Exercise:**

**Problem:**

Assume that the change in concentration of  $\text{N}_2\text{O}_4$  is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of  $\text{N}_2\text{O}_4$  with chloroform as the solvent.



(b) Confirm that the change is small enough to be neglected.

---

**Solution:**

(a)  $[\text{NO}_2] = 1.17 \times 10^{-3} M$

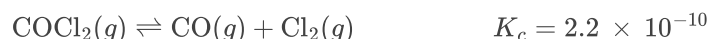
$[\text{N}_2\text{O}_4] = 0.128 M$

(b) The assumption that  $x$  is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the  $\text{N}_2\text{O}_4$  to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

**Exercise:****Problem:**

Assume that the change in concentration of  $\text{COCl}_2$  is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of  $\text{COCl}_2$  with an initial concentration of 0.3166 M.



(b) Confirm that the change is small enough to be neglected.

**Exercise:****Problem:**

Assume that the change in pressure of  $\text{H}_2\text{S}$  is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of  $\text{H}_2\text{S}$  with an initial pressure of 0.824 atm.



(b) Confirm that the change is small enough to be neglected.

---

**Solution:**

(a)  $[\text{H}_2\text{S}] = 0.810 \text{ atm}$

$[\text{H}_2] = 0.014 \text{ atm}$

$[\text{S}_2] = 0.0072 \text{ atm}$

(b) The assumption that  $2x$  is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the  $\text{H}_2\text{S}$  to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

**Exercise:****Problem:**

What are all concentrations after a mixture that contains  $[\text{H}_2\text{O}] = 1.00 M$  and  $[\text{Cl}_2\text{O}] = 1.00 M$  comes to equilibrium at 25 °C?



**Exercise:**

**Problem:**

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of  $\text{H}_2$  and 63.5 g of iodine at 448 °C.

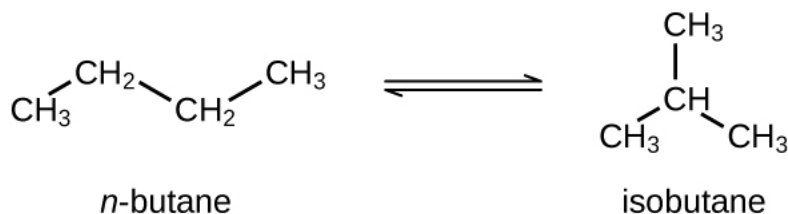


**Solution:**

507 g

**Exercise:**

**Problem:** Butane exists as two isomers, *n*-butane and isobutane.



$$K_p = 2.5 \text{ at } 25^\circ\text{C}$$

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

**Exercise:**

**Problem:**

What is the minimum mass of  $\text{CaCO}_3$  required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant ( $K_c$ ) is 0.50 for the decomposition reaction of  $\text{CaCO}_3$  at that temperature?

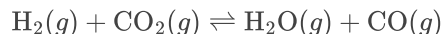


**Solution:**

330 g

**Exercise:**

**Problem:** The equilibrium constant ( $K_c$ ) for this reaction is 1.60 at 990 °C:

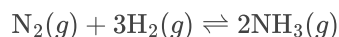


Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of  $\text{H}_2$ , 2.00 mol of  $\text{CO}_2$ , 0.750 mol of  $\text{H}_2\text{O}$ , and 1.00 mol of  $\text{CO}$  to a 5.00-L container at 990 °C.

**Exercise:**

**Problem:**

In a 3.0-L vessel, the following equilibrium partial pressures are measured:  $\text{N}_2$ , 190 torr;  $\text{H}_2$ , 317 torr;  $\text{NH}_3$ ,  $1.00 \times 10^3$  torr.

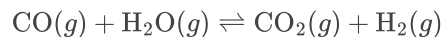


(a) How will the partial pressures of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  change if  $\text{H}_2$  is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

**Exercise:**

**Problem:** The equilibrium constant ( $K_c$ ) for this reaction is 5.0 at a given temperature.



(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of  $\text{CO}$ , 0.30 mol of water vapor, and 0.90 mol of  $\text{H}_2$  in a liter. How many moles of  $\text{CO}_2$  were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional  $\text{H}_2$  was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of  $\text{CO}$ , 0.30 mol of water vapor, and 1.2 mol of  $\text{H}_2$  in a liter. How many moles of  $\text{CO}_2$  were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

**Solution:**

(a) 0.33 mol.

(b)  $[\text{CO}]_2 = 0.50 \text{ M}$ . Added  $\text{H}_2$  forms some water as a result of a shift to the left after  $\text{H}_2$  is added.

**Exercise:**

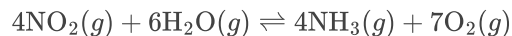
**Problem:** Antimony pentachloride decomposes according to this equation:



An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of  $\text{SbCl}_5$ , 9.14 g of  $\text{SbCl}_3$ , and 2.84 g of  $\text{Cl}_2$ . How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

**Exercise:**

**Problem:** Consider the equilibrium



(a) What is the expression for the equilibrium constant ( $K_c$ ) of the reaction?

(b) How must the concentration of  $\text{NH}_3$  change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of  $\text{NO}_2$ ?

(d) If the change in the pressure of  $\text{NO}_2$  is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of  $\text{O}_2$  change?

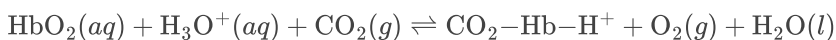
**Solution:**

(a)  $K_c = \frac{[\text{NH}_3]^4[\text{O}_2]^7}{[\text{NO}_2]^4[\text{H}_2\text{O}]^6}$ . (b)  $[\text{NH}_3]$  must increase for  $Q_c$  to reach  $K_c$ . (c) The increase in system volume would lower the partial pressures of all reactants (including  $\text{NO}_2$ ). (d)  $P_{\text{O}_2} = 49 \text{ torr}$

**Exercise:**

**Problem:**

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin ( $\text{HbO}_2$ ), is partially regulated by the concentration of  $\text{H}_3\text{O}^+$  and dissolved  $\text{CO}_2$  in the blood. Although the equilibrium is complicated, it can be summarized as



(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and  $\text{CO}_2$  in a muscle during exertion stimulates release of  $\text{O}_2$  from the oxyhemoglobin in the blood passing through the muscle.

**Exercise:**

**Problem:**

Liquid  $\text{N}_2\text{O}_3$  is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to  $\text{NO}$  and  $\text{NO}_2$ . At  $25^\circ\text{C}$ , a value of  $K_P = 1.91$  has been established for this decomposition. If 0.236 moles of  $\text{N}_2\text{O}_3$  are placed in a 1.52-L vessel at  $25^\circ\text{C}$ , calculate the equilibrium partial pressures of  $\text{N}_2\text{O}_3(g)$ ,  $\text{NO}_2(g)$ , and  $\text{NO}(g)$ .

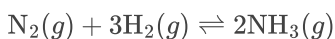
**Solution:**

$$P_{\text{N}_2\text{O}_3} = 1.90 \text{ atm and } P_{\text{NO}} = P_{\text{NO}_2} = 1.90 \text{ atm}$$

**Exercise:**

**Problem:**

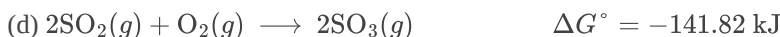
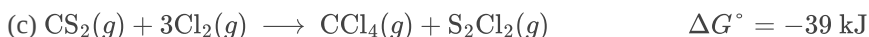
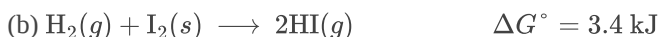
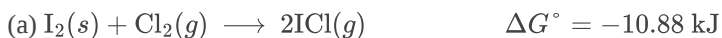
A 1.00-L vessel at  $400^\circ\text{C}$  contains the following equilibrium concentrations:  $\text{N}_2$ , 1.00 M;  $\text{H}_2$ , 0.50 M; and  $\text{NH}_3$ , 0.25 M. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M? The equilibrium reaction is



**Exercise:**

**Problem:**

Calculate the equilibrium constant at  $25^\circ\text{C}$  for each of the following reactions from the value of  $\Delta G^\circ$  given.



**Exercise:**

**Problem:** Calculate the equilibrium constant at the temperature given.

- (a)  $\text{O}_2(g) + 2\text{F}_2(g) \longrightarrow 2\text{F}_2\text{O}(g)$  ( $T = 100\text{ }^\circ\text{C}$ )
- (b)  $\text{I}_2(s) + \text{Br}_2(l) \longrightarrow 2\text{IBr}(g)$  ( $T = 0.0\text{ }^\circ\text{C}$ )
- (c)  $2\text{LiOH}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$  ( $T = 575\text{ }^\circ\text{C}$ )
- (d)  $\text{N}_2\text{O}_3(g) \longrightarrow \text{NO}(g) + \text{NO}_2(g)$  ( $T = -10.0\text{ }^\circ\text{C}$ )
- (e)  $\text{SnCl}_4(l) \longrightarrow \text{SnCl}_4(g)$  ( $T = 200\text{ }^\circ\text{C}$ )

**Solution:**

In each of the following, the value of  $\Delta G$  is not given at the temperature of the reaction. Therefore, we must calculate  $\Delta G$  from the values  $\Delta H^\circ$  and  $\Delta S$  and then calculate  $\Delta G$  from the relation  $\Delta G = \Delta H^\circ - T\Delta S^\circ$ .

- (a)  $K = 1.29$ ;  
 (b)  $K = 2.51 \times 10^{-3}$ ;  
 (c)  $K = 4.83 \times 10^3$ ;  
 (d)  $K = 0.219$ ;  
 (e)  $K = 16.1$

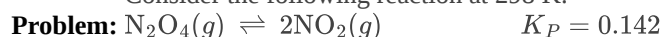
**Exercise:**

**Problem:** Calculate the equilibrium constant at the temperature given.

- (a)  $\text{I}_2(s) + \text{Cl}_2(g) \longrightarrow 2\text{ICl}(g)$  ( $T = 100\text{ }^\circ\text{C}$ )
- (b)  $\text{H}_2(g) + \text{I}_2(s) \longrightarrow 2\text{HI}(g)$  ( $T = 0.0\text{ }^\circ\text{C}$ )
- (c)  $\text{CS}_2(g) + 3\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$  ( $T = 125\text{ }^\circ\text{C}$ )
- (d)  $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g)$  ( $T = 675\text{ }^\circ\text{C}$ )
- (e)  $\text{CS}_2(g) \longrightarrow \text{CS}_2(l)$  ( $T = 90\text{ }^\circ\text{C}$ )

**Exercise:**

Consider the following reaction at 298 K:



What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

**Solution:**

The standard free energy change is  $\Delta G_{298}^\circ = -RT \ln K = 4.84\text{ kJ/mol}$ . When reactants and products are in their standard states (1 bar or 1 atm),  $Q = 1$ . As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases):  $Q < 1$ , and  $\Delta G_{298}$  becomes less positive as it approaches zero. At equilibrium,  $Q = K$ , and  $\Delta G = 0$ .

**Exercise:**

**Problem:**

Determine the normal boiling point (in kelvin) of dichloroethane,  $\text{CH}_2\text{Cl}_2$ . Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

**Exercise:**

**Problem:** Under what conditions is  $\text{N}_2\text{O}_3(g) \longrightarrow \text{NO}(g) + \text{NO}_2(g)$  spontaneous?

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**Solution:**

The reaction will be spontaneous at temperatures greater than 287 K.

**Exercise:**

**Problem:**

At room temperature, the equilibrium constant ( $K_w$ ) for the self-ionization of water is  $1.00 \times 10^{-14}$ . Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

**Exercise:**

**Problem:**

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction  $2\text{H}_2\text{S}(g) + \text{SO}_2(g) \rightleftharpoons \frac{3}{8}\text{S}_8(s, \text{ rhombic}) + 2\text{H}_2\text{O}(l)$ . What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

---

**Solution:**

$$K = 5.35 \times 10^{15}$$

The process is exothermic.

**Exercise:**

**Problem:**

Consider the decomposition of  $\text{CaCO}_3(s)$  into  $\text{CaO}(s)$  and  $\text{CO}_2(g)$ . What is the equilibrium partial pressure of  $\text{CO}_2$  at room temperature?

**Exercise:**

**Problem:**

In the laboratory, hydrogen chloride ( $\text{HCl}(g)$ ) and ammonia ( $\text{NH}_3(g)$ ) often escape from bottles of their solutions and react to form the ammonium chloride ( $\text{NH}_4\text{Cl}(s)$ ), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of  $\text{HCl}$  and  $\text{NH}_3$  in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

---

**Solution:**

$1.0 \times 10^{-8}$  atm. This is the maximum pressure of the gases under the stated conditions.

**Exercise:**

**Problem:**

Benzene can be prepared from acetylene.  $3\text{C}_2\text{H}_2(g) \rightleftharpoons \text{C}_6\text{H}_6(g)$ . Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

**Exercise:**

**Problem:**

Carbon dioxide decomposes into  $\text{CO}$  and  $\text{O}_2$  at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of  $\text{CO}_2$  was 1.15 atm?

---

**Solution:**

$$x = 1.29 \times 10^{-5} \text{ atm} = P_{\text{O}_2}$$

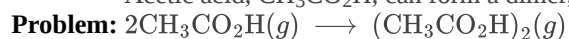
**Exercise:****Problem:**

Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.  
 $\text{CH}_4(g) + 4\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + 4\text{HCl}(g)$

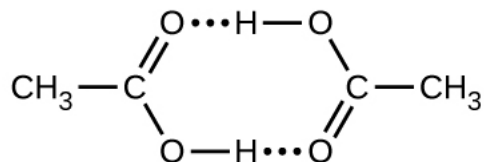
What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

**Exercise:**

Acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , can form a dimer,  $(\text{CH}_3\text{CO}_2\text{H})_2$ , in the gas phase.



The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is  $1.3 \times 10^3$  (pressure in atm). What is  $\Delta S^\circ$  for the reaction?

---

**Solution:**

$$-0.16 \text{ kJ}$$



## Introduction

class="introduction"

- Brønsted-Lowry Acids and Bases
- pH and pOH
- Relative Strengths of Acids and Bases
- Hydrolysis of Salt Solutions
- Polyprotic Acids
- Buffers
- Acid-Base Titrations

Sinkholes  
such as this  
are the result  
of reactions  
between  
acidic  
groundwater  
s and basic  
rock  
formations,  
like  
limestone.  
(credit:  
modification  
of work by  
Emil  
Kehnel)



Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water,  $\text{H}^+$  and  $\text{OH}^-$ , is widely encountered in nature and society. As introduced in another chapter of this text, acid-base chemistry involves the transfer of hydrogen ions from donors (acids) to acceptors (bases). These  $\text{H}^+$  transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation ([\[link\]](#)) to oxygen transport in the human body. This chapter will further explore acid-base chemistry with an emphasis on the equilibrium aspects of this important reaction class.

## Brønsted-Lowry Acids and Bases

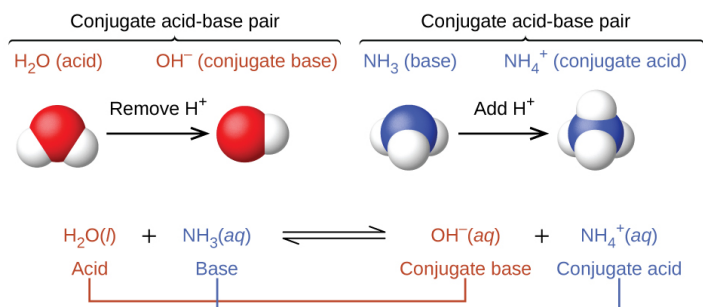
By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

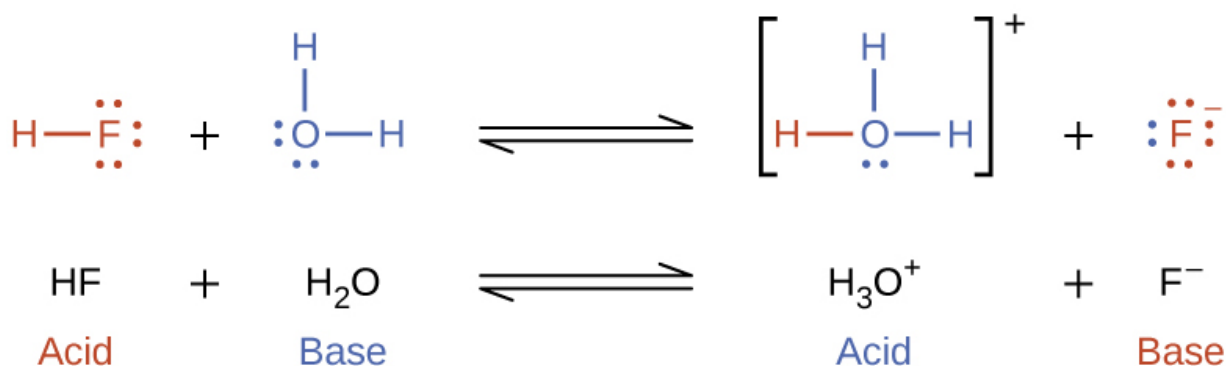
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be  $\text{CO}_2$ ), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions,  $\text{H}^+$ . (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope,  $^1\text{H}$ .) A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

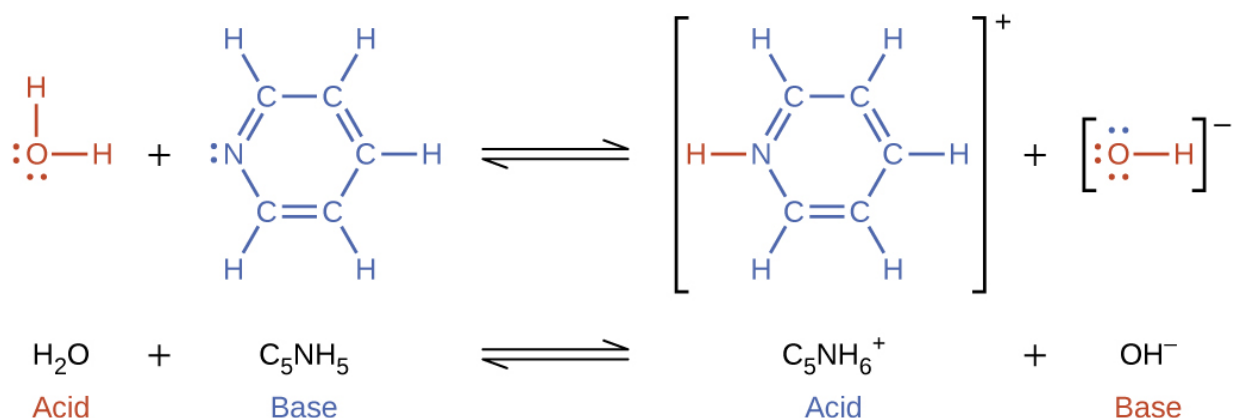
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates  $\text{H}^+$ , the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts  $\text{H}^+$ , it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion,  $\text{OH}^-$ , the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion,  $\text{NH}_4^+$ , the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



**Base ionization** of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules,  $\text{C}_5\text{NH}_5$ , undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called **amphiprotic**, or

more generally, **amphoteric**, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphotropic species, bicarbonate ion and water:

**Equation:**

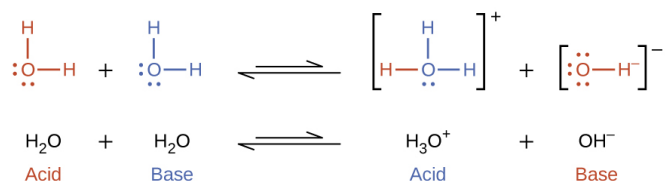


**Equation:**



The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphotropic substance can react with one another as illustrated for water in the equations below:



The process in which like molecules react to yield ions is called **autoionization**. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the **ion-product constant for water,  $K_w$** :

**Equation:**



The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C,  $K_w$  has a value of  $1.0 \times 10^{-14}$ . The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for  $K_w$  is about  $5.6 \times 10^{-13}$ , roughly 50 times larger than the value at 25 °C.

**Example:****Ion Concentrations in Pure Water**

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

**Solution**

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water,  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = x$ . At 25 °C:

**Equation:**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

**Equation:**

$$x = [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same,  $1.0 \times 10^{-7} M$ .

**Check Your Learning**

The ion product of water at 80 °C is  $2.4 \times 10^{-13}$ . What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

**Note:****Answer:**

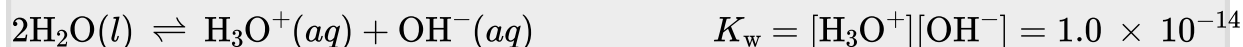
$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 4.9 \times 10^{-7} M$$

**Example:****The Inverse Relation between  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$** 

A solution of an acid in water has a hydronium ion concentration of  $2.0 \times 10^{-6} M$ . What is the concentration of hydroxide ion at 25 °C?

**Solution**

Use the value of the ion-product constant for water at 25 °C

**Equation:**

to calculate the missing equilibrium concentration.

Rearrangement of the  $K_w$  expression shows that  $[\text{OH}^-]$  is inversely proportional to  $[\text{H}_3\text{O}^+]$ :

**Equation:**

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Châtelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the  $K_w$  expression confirms this calculation, resulting in the expected value:

**Equation:**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

### Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of  $0.001\text{ M}$  at  $25\text{ }^\circ\text{C}$ ?

**Note:**

**Answer:**

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-11}\text{ M}$$

### Example:

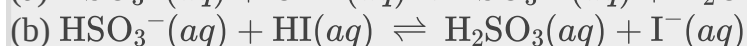
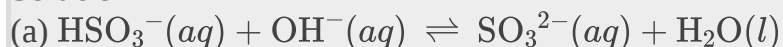
#### Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of  $\text{HSO}_3^-$

(a) as an acid with  $\text{OH}^-$

(b) as a base with  $\text{HI}$

**Solution**



### Check Your Learning

Write separate equations representing the reaction of  $\text{H}_2\text{PO}_4^-$

(a) as a base with  $\text{HBr}$

(b) as an acid with  $\text{OH}^-$

**Note:**

**Answer:**

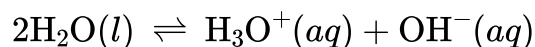
(a)  $\text{H}_2\text{PO}_4^-(aq) + \text{HBr}(aq) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{Br}^-(aq)$ ; (b)

$\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l)$

## Key Concepts and Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion,  $\text{H}_3\text{O}^+$ , and the hydroxide ion,  $\text{OH}^-$  when it undergoes autoionization:

**Equation:**



The ion product of water,  $K_w$  is the equilibrium constant for the autoionization reaction:

**Equation:**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

## Key Equations



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Write equations that show  $\text{NH}_3$  as both a conjugate acid and a conjugate base.

#### Solution:

One example for  $\text{NH}_3$  as a conjugate acid:  $\text{NH}_2^- + \text{H}^+ \longrightarrow \text{NH}_3$ ; as a conjugate base:  $\text{NH}_4^+(aq) + \text{OH}^-(aq) \longrightarrow \text{NH}_3(aq) + \text{H}_2\text{O}(l)$

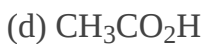
### Exercise:

**Problem:** Write equations that show  $\text{H}_2\text{PO}_4^-$  acting both as an acid and as a base.

### Exercise:

#### Problem:

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:



#### Solution:

(a)  $\text{H}_3\text{O}^+(aq) \longrightarrow \text{H}^+(aq) + \text{H}_2\text{O}(l)$ ; (b)  $\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$ ; (c)  $\text{NH}_3(aq) \longrightarrow \text{H}^+(aq) + \text{NH}_2^-(aq)$ ; (d)  $\text{CH}_3\text{CO}_2\text{H}(aq) \longrightarrow \text{H}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)$ ; (e)  $\text{NH}_4^+(aq) \longrightarrow \text{H}^+(aq) + \text{NH}_3(aq)$ ; (f)  $\text{HSO}_4^-(aq) \longrightarrow \text{H}^+(aq) + \text{SO}_4^{2-}(aq)$

### Exercise:

**Problem:**

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

- (a)  $\text{HNO}_3$
- (b)  $\text{PH}_4^+$
- (c)  $\text{H}_2\text{S}$
- (d)  $\text{CH}_3\text{CH}_2\text{COOH}$
- (e)  $\text{H}_2\text{PO}_4^-$
- (f)  $\text{HS}^-$

**Exercise:****Problem:**

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- (a)  $\text{H}_2\text{O}$
- (b)  $\text{OH}^-$
- (c)  $\text{NH}_3$
- (d)  $\text{CN}^-$
- (e)  $\text{S}^{2-}$
- (f)  $\text{H}_2\text{PO}_4^-$

---

**Solution:**

- (a)  $\text{H}_2\text{O}(l) + \text{H}^+(aq) \longrightarrow \text{H}_3\text{O}^+(aq)$ ; (b)  $\text{OH}^-(aq) + \text{H}^+(aq) \longrightarrow \text{H}_2\text{O}(l)$ ;  
(c)  $\text{NH}_3(aq) + \text{H}^+(aq) \longrightarrow \text{NH}_4^+(aq)$ ; (d)  $\text{CN}^-(aq) + \text{H}^+(aq) \longrightarrow \text{HCN}(aq)$ ; (e)  $\text{S}^{2-}(aq) + \text{H}^+(aq) \longrightarrow \text{HS}^-(aq)$ ; (f)  $\text{H}_2\text{PO}_4^-(aq) + \text{H}^+(aq) \longrightarrow \text{H}_3\text{PO}_4(aq)$

**Exercise:**

**Problem:**

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

- (a)  $\text{HS}^-$
- (b)  $\text{PO}_4^{3-}$
- (c)  $\text{NH}_2^-$
- (d)  $\text{C}_2\text{H}_5\text{OH}$
- (e)  $\text{O}^{2-}$
- (f)  $\text{H}_2\text{PO}_4^-$

**Exercise:****Problem:**

What is the conjugate acid of each of the following? What is the conjugate base of each?

- (a)  $\text{OH}^-$
- (b)  $\text{H}_2\text{O}$
- (c)  $\text{HCO}_3^-$
- (d)  $\text{NH}_3$
- (e)  $\text{HSO}_4^-$
- (f)  $\text{H}_2\text{O}_2$
- (g)  $\text{HS}^-$
- (h)  $\text{H}_5\text{N}_2^+$

---

**Solution:**

(a)  $\text{H}_2\text{O}$ ,  $\text{O}^{2-}$ ; (b)  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ; (c)  $\text{H}_2\text{CO}_3$ ,  $\text{CO}_3^{2-}$ ; (d)  $\text{NH}_4^+$ ,  $\text{NH}_2^-$ ; (e)  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_4^{2-}$ ; (f)  $\text{H}_3\text{O}_2^+$ ,  $\text{HO}_2^-$ ; (g)  $\text{H}_2\text{S}$ ;  $\text{S}^{2-}$ ; (h)  $\text{H}_6\text{N}_2^{2+}$ ,  $\text{H}_4\text{N}_2$

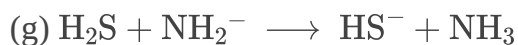
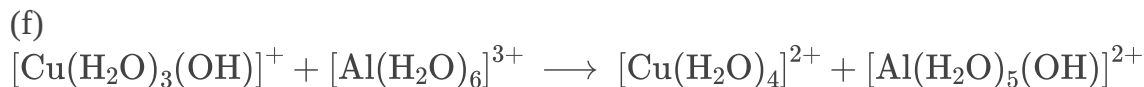
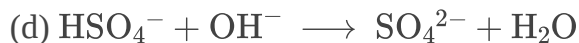
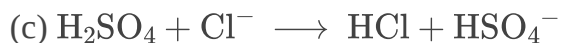
**Exercise:**

**Problem:**

What is the conjugate acid of each of the following? What is the conjugate base of each?

**Exercise:****Problem:**

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

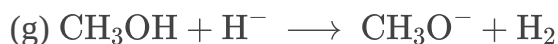
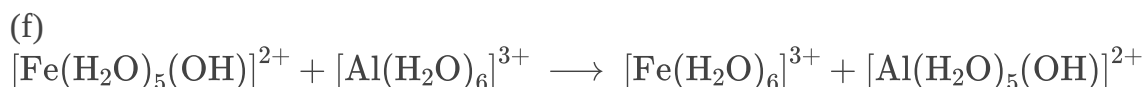
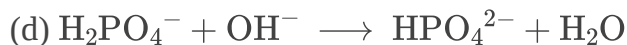
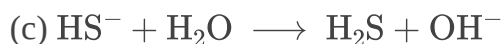
**Solution:**

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a)  $\text{HNO}_3(\text{BA})$ ,  $\text{H}_2\text{O}(\text{BB})$ ,  $\text{H}_3\text{O}^+(\text{CA})$ ,  $\text{NO}_3^-(\text{CB})$ ; (b)  $\text{CN}^-(\text{BB})$ ,  $\text{H}_2\text{O}(\text{BA})$ ,  $\text{HCN}(\text{CA})$ ,  $\text{OH}^-(\text{CB})$ ; (c)  $\text{H}_2\text{SO}_4(\text{BA})$ ,  $\text{Cl}^-(\text{BB})$ ,  $\text{HCl}(\text{CA})$ ,  $\text{HSO}_4^-(\text{CB})$ ; (d)  $\text{HSO}_4^-(\text{BA})$ ,  $\text{OH}^-(\text{BB})$ ,  $\text{SO}_4^{2-}(\text{CB})$ ,  $\text{H}_2\text{O}(\text{CA})$ ; (e)  $\text{O}^{2-}(\text{BB})$ ,  $\text{H}_2\text{O}(\text{BA})$ ,  $\text{OH}^-(\text{CB and CA})$ ; (f)  $[\text{Cu}(\text{H}_2\text{O})_3(\text{OH})]^+(\text{BB})$ ,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{BA})$ ,  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}(\text{CA})$ ,  $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{CB})$ ; (g)  $\text{H}_2\text{S}(\text{BA})$ ,  $\text{NH}_2^-(\text{BB})$ ,  $\text{HS}^-(\text{CB})$ ,  $\text{NH}_3(\text{CA})$

### Exercise:

#### Problem:

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

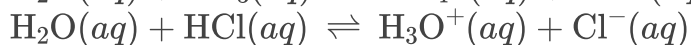


### Exercise:

**Problem:** What are amphoteric species? Illustrate with suitable equations.

#### Solution:

Amphoteric species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is  $\text{H}_2\text{O}$ . As an acid:



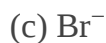
### Exercise:

**Problem:**

State which of the following species are amphoteric and write chemical equations illustrating the amphoteric character of these species:

**Exercise:****Problem:**

State which of the following species are amphoteric and write chemical equations illustrating the amphoteric character of these species.



---

**Solution:**

amphoteric: (a)  $\text{NH}_3 + \text{H}_3\text{O}^+ \longrightarrow \text{NH}_4\text{OH} + \text{H}_2\text{O}$ ,

$\text{NH}_3 + \text{OCH}_3^- \longrightarrow \text{NH}_2^- + \text{CH}_3\text{OH}$ ; (b)

$\text{HPO}_4^{2-} + \text{OH}^- \longrightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$ ,

$\text{HPO}_4^{2-} + \text{HClO}_4 \longrightarrow \text{H}_2\text{PO}_4^- + \text{ClO}_4^-$ ; not amphoteric: (c)  $\text{Br}^-$ ; (d)  $\text{NH}_4^+$ ;

(e)  $\text{AsO}_4^{3-}$

**Exercise:****Problem:**

Is the self-ionization of water endothermic or exothermic? The ionization constant for water ( $K_w$ ) is  $2.9 \times 10^{-14}$  at 40 °C and  $9.3 \times 10^{-14}$  at 60 °C.

## Glossary

### acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

### amphiprotic

species that may either donate or accept a proton in a Bronsted-Lowry acid-base reaction

### amphoteric

species that can act as either an acid or a base

### autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

### base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

### Brønsted-Lowry acid

proton donor

### Brønsted-Lowry base

proton acceptor

### conjugate acid

substance formed when a base gains a proton

### conjugate base

substance formed when an acid loses a proton

### ion-product constant for water ( $K_w$ )

equilibrium constant for the autoionization of water

## pH and pOH

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water ( $K_w$ ). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where “X” is the quantity of interest and “log” is the base-10 logarithm:

**Equation:**

$$\text{pX} = -\log X$$

The **pH** of a solution is therefore defined as shown here, where  $[\text{H}_3\text{O}^+]$  is the molar concentration of hydronium ion in the solution:

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$



Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

**Equation:**

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH:**

**Equation:**

$$\text{pOH} = -\log[\text{OH}^-]$$

or

**Equation:**

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the  $K_w$  expression:

**Equation:**

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

**Equation:**

$$-\log K_w = -\log ([\text{H}_3\text{O}^+] [\text{OH}^-]) = -\log[\text{H}_3\text{O}^+] + -\log[\text{OH}^-]$$

**Equation:**

$$\text{p}K_w = \text{pH} + \text{pOH}$$

At 25 °C, the value of  $K_w$  is  $1.0 \times 10^{-14}$ , and so:

**Equation:**

$$14.00 = \text{pH} + \text{pOH}$$

As was shown in [\[link\]](#), the hydronium ion molarity in pure water (or any neutral solution) is  $1.0 \times 10^{-7} M$  at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00$$

**Equation:**

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than  $1.0 \times 10^{-7} M$  and hydroxide ion molarities less than  $1.0 \times 10^{-7} M$  (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than  $1.0 \times 10^{-7} M$  and hydroxide ion molarities greater than  $1.0 \times 10^{-7} M$  (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant  $K_w$  is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the “Check Your Learning” exercise accompanying [\[link\]](#) showed the hydronium molarity of pure water at 80 °C is  $4.9 \times 10^{-7} M$ , which corresponds to pH and pOH values of:

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.9 \times 10^{-7}) = 6.31$$

**Equation:**

$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit  $\text{pH} = \text{pOH} = 6.31$ , acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas

basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C ([\[link\]](#)).

Summary of Relations for Acidic, Basic and Neutral Solutions		
Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

[\[link\]](#) shows the relationships between  $[H_3O^+]$ ,  $[OH^-]$ , pH, and pOH for solutions classified as acidic, basic, and neutral.

$[\text{H}_3\text{O}^+]$ (M)	$[\text{OH}^-]$ (M)	pH	pOH	Sample Solution	
$10^1$	$10^{-15}$	-1	15		
$10^0$ or 1	$10^{-14}$	0	14	← 1 M HCl	acidic
$10^{-1}$	$10^{-13}$	1	13	← gastric juice	
$10^{-2}$	$10^{-12}$	2	12	← lime juice	
$10^{-3}$	$10^{-11}$	3	11	← 1 M $\text{CH}_3\text{CO}_2\text{H}$ (vinegar)	
$10^{-4}$	$10^{-10}$	4	10	← stomach acid	
$10^{-5}$	$10^{-9}$	5	9	← wine	
$10^{-6}$	$10^{-8}$	6	8	← orange juice	
$10^{-7}$	$10^{-7}$	7	7	← coffee	
$10^{-8}$	$10^{-6}$	8	6	← rain water	
$10^{-9}$	$10^{-5}$	9	5	← pure water	neutral
$10^{-10}$	$10^{-4}$	10	4	← blood	
$10^{-11}$	$10^{-3}$	11	3	← ocean water	
$10^{-12}$	$10^{-2}$	12	2	← baking soda	
$10^{-13}$	$10^{-1}$	13	1	← Milk of Magnesia	
$10^{-14}$	$10^0$ or 1	14	0	← household ammonia, $\text{NH}_3$	
$10^{-15}$	$10^1$	15	-1	← bleach	
				← 1 M NaOH	basic

The pH and pOH scales represent concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

### Example:

#### Calculation of pH from $[\text{H}_3\text{O}^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of  $1.2 \times 10^{-3} \text{ M}$ ?

#### Solution

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

**Equation:**

$$= -\log(1.2 \times 10^{-3})$$

**Equation:**

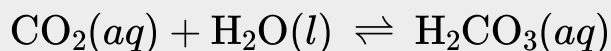
$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in [Appendix B](#). When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

### **Check Your Learning**

Water exposed to air contains carbonic acid,  $\text{H}_2\text{CO}_3$ , due to the reaction between carbon dioxide and water:

**Equation:**



Air-saturated water has a hydronium ion concentration caused by the dissolved  $\text{CO}_2$  of  $2.0 \times 10^{-6} M$ , about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

**Note:**

**Answer:**

5.70

**Example:**

### Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

**Solution**

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.3$$

**Equation:**

$$\log[\text{H}_3\text{O}^+] = -7.3$$

**Equation:**

$$[\text{H}_3\text{O}^+] = 10^{-7.3} \text{ or } [\text{H}_3\text{O}^+] = \text{antilog of } -7.3$$

**Equation:**

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8} M$$

(On a calculator take the antilog, or the “inverse” log, of  $-7.3$ , or calculate  $10^{-7.3}$ .)

### Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of  $-1.07$ .

**Note:**

**Answer:**

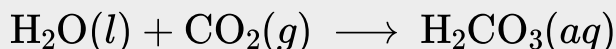
$12 M$

**Note:**

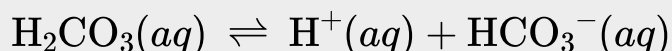
## Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved  $\text{CO}_2$  which forms carbonic acid:

**Equation:**

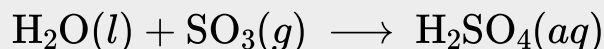


**Equation:**



Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

**Equation:**



**Equation:**

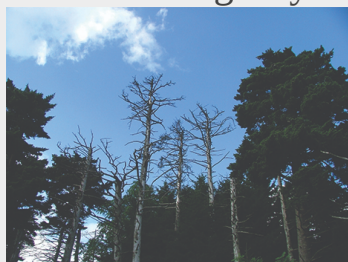


Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes

uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone ([\[link\]](#)). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this [website](#) hosted by the US Environmental Protection Agency.



(a)



(b)

(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also corrodes statues that are carved from marble or limestone.

(credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

### **Example:**

#### **Calculation of pOH**

What are the pOH and the pH of a 0.0125-*M* solution of potassium hydroxide, KOH?

#### **Solution**

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding  $[\text{OH}^-] = 0.0125 \text{ M}$ :

#### **Equation:**



$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0125$$

**Equation:**

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

**Equation:**

$$\text{pH} + \text{pOH} = 14.00$$

**Equation:**

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

### Check Your Learning

The hydronium ion concentration of vinegar is approximately  $4 \times 10^{-3} \text{ M}$ . What are the corresponding values of pOH and pH?

**Note:**

**Answer:**

$$\text{pOH} = 11.6, \text{pH} = 2.4$$

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter ([\[link\]](#)).



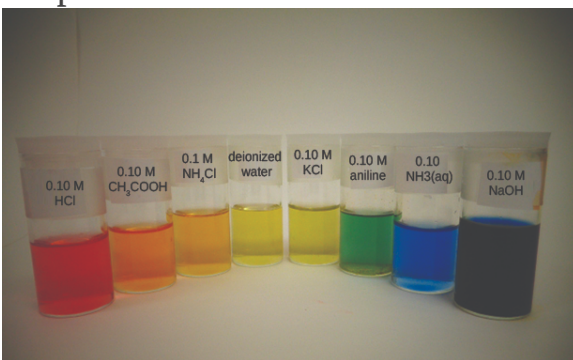
(a)



(b)

(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of  $\pm 0.002$  pH units, and may cost in excess of \$1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy ( $\pm 0.2$  pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators ([link](#)). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.



(a)



(b)

(a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions. (credit: modification of work by Sahar Atwa)

## Key Concepts and Summary

Concentrations of hydronium and hydroxide ions in aqueous media are often represented as logarithmic pH and pOH values, respectively. At 25 °C, the autoprotolysis equilibrium for water requires the sum of pH and pOH to equal 14 for any aqueous solution. The relative concentrations of hydronium and hydroxide ion in a solution define its status as acidic ( $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ ), basic ( $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ ), or neutral ( $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ). At 25 °C, a pH < 7 indicates an acidic solution, a pH > 7 a basic solution, and a pH = 7 a neutral solution.

## Key Equations

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

$$\text{pH} + \text{pOH} = \text{p}K_{\text{w}} = 14.00 \text{ at } 25\text{ }^\circ\text{C}$$

## Chemistry End of Chapter Exercises

### Exercise:

#### Problem:

Explain why a sample of pure water at 40 °C is neutral even though  $[\text{H}_3\text{O}^+] = 1.7 \times 10^{-7} \text{ M}$ .  $K_w$  is  $2.9 \times 10^{-14}$  at 40 °C.

---

#### Solution:

In a neutral solution  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . At 40 °C,  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = (2.910 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$ .

### Exercise:

#### Problem:

The ionization constant for water ( $K_w$ ) is  $2.9 \times 10^{-14}$  at 40 °C. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH for pure water at 40 °C.

### Exercise:

#### Problem:

The ionization constant for water ( $K_w$ ) is  $9.311 \times 10^{-14}$  at 60 °C. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH for pure water at 60 °C.

---

#### Solution:

$$x = 3.051 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]; \text{pH} = -\log 3.051 \times 10^{-7} = -(-6.5156) = 6.5156; \text{pOH} = \text{pH} = 6.5156$$

### Exercise:

#### Problem:

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 M HCl

(b) 0.0143 M NaOH

(c) 3.0 M HNO<sub>3</sub>

(d) 0.0031 M Ca(OH)<sub>2</sub>

**Exercise:**

**Problem:**

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 M HClO<sub>4</sub>

(b) 0.21 M NaOH

(c) 0.000071 M Ba(OH)<sub>2</sub>

(d) 2.5 M KOH

---

**Solution:**

(a) pH = 3.587; pOH = 10.413; (b) pH = 0.68; pOH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pH = -0.40; pOH = 14.4

**Exercise:**

**Problem:**

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

**Exercise:**

**Problem:**

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

---

**Solution:**

$$[\text{H}_3\text{O}^+] = 3.0 \times 10^{-7} \text{ M}; [\text{OH}^-] = 3.3 \times 10^{-8} \text{ M}$$

**Exercise:****Problem:**

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See [\[link\]](#) for useful information.

**Exercise:****Problem:**

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See [\[link\]](#) for useful information.

---

**Solution:**

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-2} \text{ M}; [\text{OH}^-] = 1 \times 10^{-12} \text{ M}$$

**Exercise:****Problem:**

The hydronium ion concentration in a sample of rainwater is found to be  $1.7 \times 10^{-6} \text{ M}$  at 25 °C. What is the concentration of hydroxide ions in the rainwater?

**Exercise:****Problem:**

The hydroxide ion concentration in household ammonia is  $3.2 \times 10^{-3} \text{ M}$  at 25 °C. What is the concentration of hydronium ions in the solution?

---

**Solution:**

$$[\text{OH}^-] = 3.1 \times 10^{-12} \text{ M}$$

## Glossary

acidic

a solution in which  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

basic

a solution in which  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

neutral

describes a solution in which  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

## Relative Strengths of Acids and Bases

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

## Acid and Base Ionization Constants

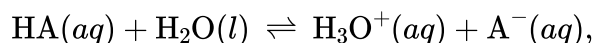
The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in [\[link\]](#).

6 Strong Acids		6 Strong Bases	
HClO <sub>4</sub>	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	Ca(OH) <sub>2</sub>	calcium hydroxide
HNO <sub>3</sub>	nitric acid	Sr(OH) <sub>2</sub>	strontium hydroxide
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid	Ba(OH) <sub>2</sub>	barium hydroxide

Some of the common strong acids and bases are listed here.

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant,  $K_a$** . For the reaction of an acid HA:

**Equation:**



the acid ionization constant is written

**Equation:**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

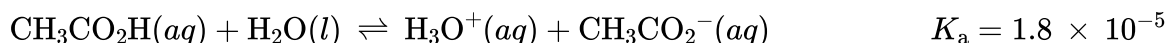
where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include  $[\text{H}_2\text{O}]$  in the equation. The larger the  $K_a$  of an acid, the larger the concentration of  $\text{H}_3\text{O}^+$  and  $\text{A}^-$  relative to the concentration of the nonionized acid, HA,



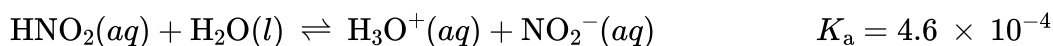
in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ( $K_a \approx \infty$ ). Acids that are partially ionized are called “weak,” and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in [Appendix H](#).

To illustrate this idea, three acid ionization equations and  $K_a$  values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order  $\text{CH}_3\text{CO}_2\text{H} < \text{HNO}_2 < \text{HSO}_4^-$ :

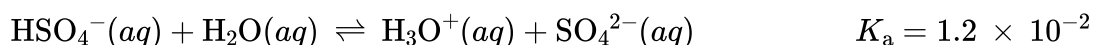
**Equation:**



**Equation:**



**Equation:**



Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is defined in terms of the composition of an equilibrium mixture:

**Equation:**

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry,  $[\text{A}^-] = [\text{H}_3\text{O}^+]$ ). Unlike the  $K_a$  value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

**Example:**

**Calculation of Percent Ionization from pH**

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

**Solution**

The percent ionization for an acid is:

**Equation:**

$$\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HNO}_2]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

**Equation:**

$$[\text{H}_3\text{O}^+] = 10^{-2.09} = 0.0081 \text{ M}$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

**Equation:**

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5 \%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

**Check Your Learning**

Calculate the percent ionization of a 0.10-M solution of acetic acid with a pH of 2.89.

**Note:**

**Answer:**

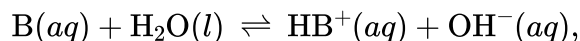
1.3% ionized

**Note:**

View the [simulation](#) of strong and weak acids and bases at the molecular level.

Just as for acids, the relative strength of a base is reflected in the magnitude of its **base-ionization constant ( $K_b$ )** in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

**Equation:**

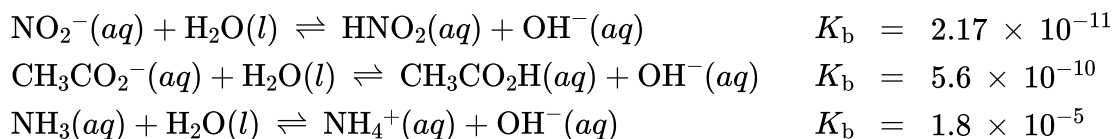


the ionization constant is written as

**Equation:**

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order  $\text{NO}_2^- < \text{CH}_2\text{CO}_2^- < \text{NH}_3$ .

**Equation:**

A table of ionization constants for weak bases appears in [Appendix I](#). As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

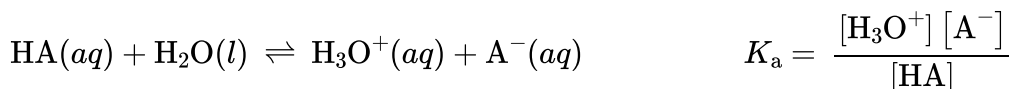
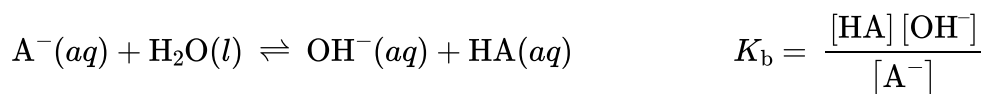
**Equation:**

$$\% \text{ ionization} = [\text{OH}^-]_{eq} / [\text{B}]_0 \times 100 \%$$

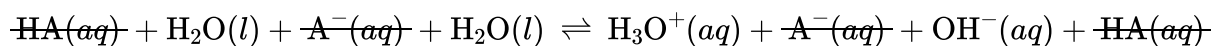
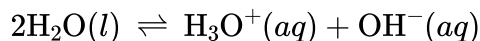
but will vary depending on the base ionization constant and the initial concentration of the solution.

**Relative Strengths of Conjugate Acid-Base Pairs**

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant,  $K_a$  or  $K_b$ , which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair  $\text{HA} / \text{A}^-$ , ionization equilibrium equations and ionization constant expressions are

**Equation:****Equation:**

Adding these two chemical equations yields the equation for the autoionization for water:

**Equation:****Equation:**

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

**Equation:**

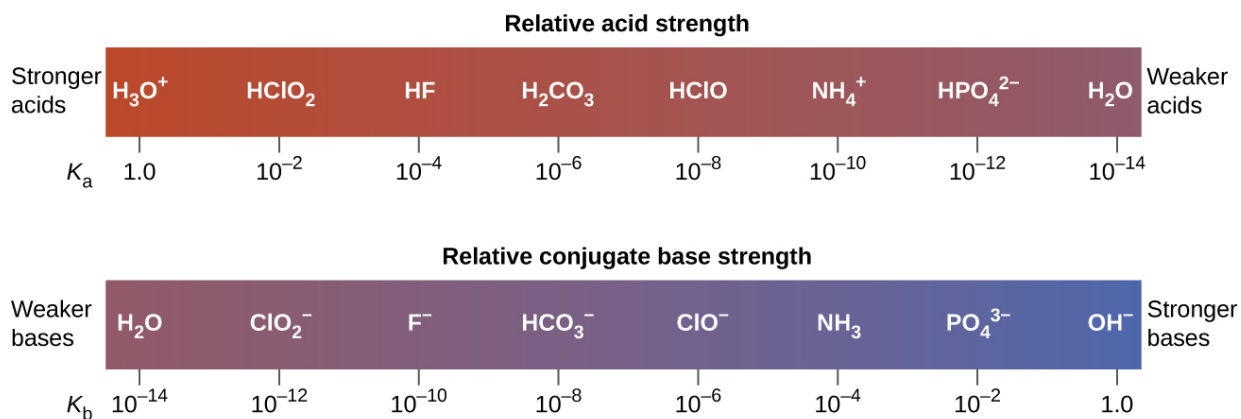
$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water,  $K_w$ . By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:



**Equation:**

$$K_a = K_w/K_b \text{ or } K_b = K_w/K_a$$

The inverse proportional relation between  $K_a$  and  $K_b$  means *the stronger the acid or base, the weaker its conjugate partner*. [\[link\]](#) illustrates this relation for several conjugate acid-base pairs.



Relative strengths of several conjugate acid-base pairs are shown.

Acid			Base		
	perchloric acid	$\text{HClO}_4$	Do not undergo base ionization in water	$\text{ClO}_4^-$	perchlorate ion
	sulfuric acid	$\text{H}_2\text{SO}_4$		$\text{HSO}_4^-$	hydrogen sulfate ion
	hydrogen iodide	$\text{HI}$		$\text{I}^-$	iodide ion
	hydrogen bromide	$\text{HBr}$		$\text{Br}^-$	bromide ion
	hydrogen chloride	$\text{HCl}$		$\text{Cl}^-$	chloride ion
	nitric acid	$\text{HNO}_3$	Undergo complete acid ionization in water	$\text{NO}_3^-$	nitrate ion
	hydronium ion	$\text{H}_3\text{O}^+$		$\text{H}_2\text{O}$	water
	hydrogen sulfate ion	$\text{HSO}_4^-$		$\text{SO}_4^{2-}$	sulfate ion
	phosphoric acid	$\text{H}_3\text{PO}_4$		$\text{H}_2\text{PO}_4^-$	dihydrogen phosphate ion
	hydrogen fluoride	$\text{HF}$		$\text{F}^-$	fluoride ion
	nitrous acid	$\text{HNO}_2$		$\text{NO}_2^-$	nitrite ion
	acetic acid	$\text{CH}_3\text{CO}_2\text{H}$		$\text{CH}_3\text{CO}_2^-$	acetate ion
	carbonic acid	$\text{H}_2\text{CO}_3$		$\text{HCO}_3^-$	hydrogen carbonate ion
	hydrogen sulfide	$\text{H}_2\text{S}$		$\text{HS}^-$	hydrogen sulfide ion
	ammonium ion	$\text{NH}_4^+$		$\text{NH}_3$	ammonia
	hydrogen cyanide	$\text{HCN}$		$\text{CN}^-$	cyanide ion
	hydrogen carbonate ion	$\text{HCO}_3^-$		$\text{CO}_3^{2-}$	carbonate ion
	water	$\text{H}_2\text{O}$		$\text{OH}^-$	hydroxide ion
	hydrogen sulfide ion	$\text{HS}^-$	Do not undergo acid ionization in water	$\text{S}^{2-}$	sulfide ion
	ethanol	$\text{C}_2\text{H}_5\text{OH}$		$\text{C}_2\text{H}_5\text{O}^-$	ethoxide ion
	ammonia	$\text{NH}_3$		$\text{NH}_2^-$	amide ion
	hydrogen	$\text{H}_2$		$\text{H}^-$	hydride ion
	methane	$\text{CH}_4$		$\text{CH}_3^-$	methide ion
					

This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

The listing of conjugate acid–base pairs shown in [\[link\]](#) is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table’s columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, whereas those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole

acid species present in an aqueous solution of any strong acid is  $\text{H}_3\text{O}^+(\text{aq})$ , meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for “strong” acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be “weak,” and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing  $\text{HCl} < \text{HBr} < \text{HI}$ ).

The right column of [\[link\]](#) lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don’t undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large  $K_a$ , and so its conjugate base will exhibit a  $K_b$  that is essentially zero:

strong acid :  $K_a \approx \infty$   
 conjugate base :  $K_b = K_w/K_a = K_w/\infty \approx 0$

A similar approach can be used to support the observation that conjugate acids of strong bases ( $K_b \approx \infty$ ) are of negligible strength ( $K_a \approx 0$ ).

### Example:

#### Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the  $K_b$  for the nitrite ion,  $\text{NO}_2^-$ , to calculate the  $K_a$  for its conjugate acid.

#### Solution

$K_b$  for  $\text{NO}_2^-$  is given in this section as  $2.17 \times 10^{-11}$ . The conjugate acid of  $\text{NO}_2^-$  is  $\text{HNO}_2$ ;  $K_a$  for  $\text{HNO}_2$  can be calculated using the relationship:

#### Equation:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for  $K_a$  yields

#### Equation:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the  $K_a$  for  $\text{HNO}_2$  in [Appendix H](#).

### Check Your Learning

Determine the relative acid strengths of  $\text{NH}_4^+$  and HCN by comparing their ionization constants. The ionization constant of HCN is given in [Appendix H](#) as  $4.9 \times 10^{-10}$ . The ionization constant of  $\text{NH}_4^+$  is not listed, but the ionization constant of its conjugate base,  $\text{NH}_3$ , is listed as  $1.8 \times 10^{-5}$ .

**Note:**

**Answer:**

$\text{NH}_4^+$  is the slightly stronger acid ( $K_a$  for  $\text{NH}_4^+ = 5.6 \times 10^{-10}$ ).

## Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.





**Example:****Determination of  $K_a$  from Equilibrium Concentrations**

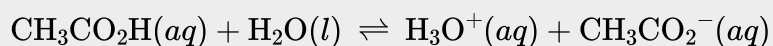
Acetic acid is the principal ingredient in vinegar ([link](#)) that provides its sour taste. At equilibrium, a solution contains  $[\text{CH}_3\text{CO}_2\text{H}] = 0.0787\text{ M}$  and  $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-] = 0.00118\text{ M}$ . What is the value of  $K_a$  for acetic acid?



Vinegar contains acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

**Solution**

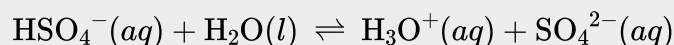
The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the  $K_a$  for acetic acid.

**Equation:****Equation:**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

**Check Your Learning**

The  $\text{HSO}_4^-$  ion, weak acid used in some household cleansers:

**Equation:**



What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition:  $[\text{H}_3\text{O}^+] = 0.027\text{ M}$ ;  $[\text{HSO}_4^-] = 0.29\text{ M}$ ; and  $[\text{SO}_4^{2-}] = 0.13\text{ M}$ ?

**Note:**

**Answer:**

$$K_a \text{ for } \text{HSO}_4^- = 1.2 \times 10^{-2}$$

**Example:**

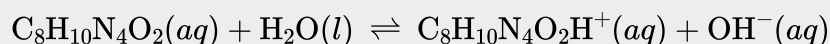
**Determination of  $K_b$  from Equilibrium Concentrations**

Caffeine,  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$  is a weak base. What is the value of  $K_b$  for caffeine if a solution at equilibrium has  $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2] = 0.050\text{ M}$ ,  $[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+] = 5.0 \times 10^{-3}\text{ M}$ , and  $[\text{OH}^-] = 2.5 \times 10^{-3}\text{ M}$ ?

**Solution**

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the  $K_b$  for caffeine.

**Equation:**



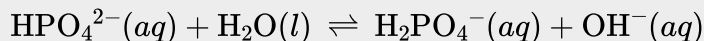
**Equation:**

$$K_b = \frac{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+][\text{OH}^-]}{[\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

**Check Your Learning**

What is the equilibrium constant for the ionization of the  $\text{HPO}_4^{2-}$  ion, a weak base

**Equation:**



if the composition of an equilibrium mixture is as follows:  $[\text{OH}^-] = 1.3 \times 10^{-6}\text{ M}$ ;  $[\text{H}_2\text{PO}_4^-] = 0.042\text{ M}$ ; and  $[\text{HPO}_4^{2-}] = 0.341\text{ M}$ ?

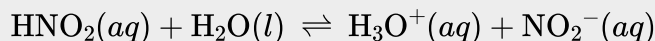
**Note:**

**Answer:**

$$K_b \text{ for } \text{HPO}_4^{2-} = 1.6 \times 10^{-7}$$

**Example:****Determination of  $K_a$  or  $K_b$  from pH**

The pH of a 0.0516-M solution of nitrous acid,  $\text{HNO}_2$ , is 2.34. What is its  $K_a$ ?

**Equation:****Solution**

The nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as “initial” values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of  $\text{H}_3\text{O}^+$  is present ( $1 \times 10^{-7} \text{ M}$ ) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an “equilibrium” value for the ICE table:

**Equation:**

$$[\text{H}_3\text{O}^+] = 10^{-2.34} = 0.0046 \text{ M}$$

The ICE table for this system is then

	$\text{HNO}_2$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{NO}_2^-$
Initial concentration (M)	0.0516				~0		0
Change (M)	-0.0046				+0.0046		+0.0046
Equilibrium concentration (M)	0.0470				0.0046		0.0046

Finally, calculate the value of the equilibrium constant using the data in the table:

**Equation:**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

**Check Your Learning.**

The pH of a solution of household ammonia, a 0.950-M solution of  $\text{NH}_3$ , is 11.612. What is  $K_b$  for  $\text{NH}_3$ .

**Note:****Answer:**

$$K_b = 1.8 \times 10^{-5}$$

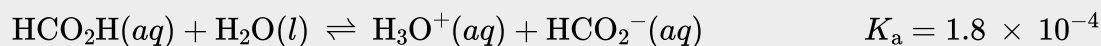
**Example:****Calculating Equilibrium Concentrations in a Weak Acid Solution**

Formic acid,  $\text{HCO}_2\text{H}$ , is one irritant that causes the body's reaction to some ant bites and stings ([link](#)).



The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH of a 0.534-M solution of formic acid?

**Equation:****Solution**

The ICE table for this system is

	$\text{HCO}_2\text{H}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{HCO}_2^-$
Initial concentration (M)	0.534				$\sim 0$		0
Change (M)					$+x$		$+x$
Equilibrium concentration (M)	$0.534 - x$				$x$		$x$

Substituting the equilibrium concentration terms into the  $K_a$  expression gives

**Equation:**

$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

**Equation:**

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying

assumption that  $x$  will be much lesser than 0.534, and so the equation becomes

**Equation:**

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for  $x$  yields

**Equation:**

$$x^2 = 0.534 \times (1.8 \times 10^{-4}) = 9.6 \times 10^{-5}$$

**Equation:**

$$x = \sqrt{9.6 \times 10^{-5}}$$

**Equation:**

$$= 9.8 \times 10^{-3} M$$

To check the assumption that  $x$  is small compared to 0.534, its relative magnitude can be estimated:

**Equation:**

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} (1.8\% \text{ of } 0.534)$$

Because  $x$  is less than 5% of the initial concentration, the assumption is valid.

As defined in the ICE table,  $x$  is equal to the equilibrium concentration of hydronium ion:

**Equation:**

$$x = [\text{H}_3\text{O}^+] = 0.0098 M$$

Finally, the pH is calculated to be

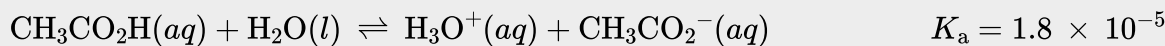
**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0098) = 2.01$$

### Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100- $M$  solution of acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ ?

**Equation:**



**Note:**

**Answer:**

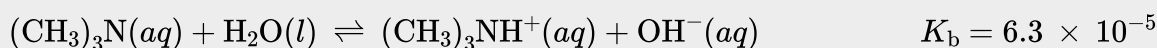
percent ionization = 1.3%

**Example:**

**Calculating Equilibrium Concentrations in a Weak Base Solution**

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-M solution of trimethylamine, a weak base:

**Equation:**



**Solution**

The ICE table for this system is

	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$			
Initial concentration (M)	0.25		0	~0
Change (M)	-x		x	x
Equilibrium concentration (M)	0.25 + (-x)		0 + x	~0 + x

Substituting the equilibrium concentration terms into the  $K_b$  expression gives

**Equation:**

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming  $x \ll 0.25$  and solving for  $x$  yields

**Equation:**

$$x = 4.0 \times 10^{-3} M$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified.

As defined in the ICE table,  $x$  is equal to the equilibrium concentration of hydroxide ion:

**Equation:**

$$[\text{OH}^-] = \sim 0 + x = x = 4.0 \times 10^{-3} M$$

**Equation:**

$$= 4.0 \times 10^{-3} M$$

The pOH is calculated to be

**Equation:**

$$\text{pOH} = -\log(4.0 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

**Equation:**

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

permits the computation of pH:

**Equation:**

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

### Check Your Learning

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-*M* solution of ammonia, a weak base with a  $K_b$  of  $1.76 \times 10^{-5}$ .

**Note:**

**Answer:**

$7.56 \times 10^{-4} M$ , 2.33%

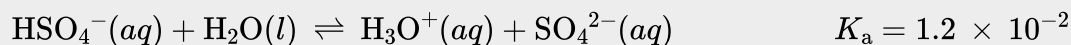
In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that  $x$  is negligible can not be made. Calculations of this sort are demonstrated in [\[link\]](#) below.

### Example:

#### Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate,  $\text{NaHSO}_4$ , is used in some household cleansers as a source of the  $\text{HSO}_4^-$  ion, a weak acid. What is the pH of a 0.50-*M* solution of  $\text{HSO}_4^-$ ?

**Equation:**



**Solution**

The ICE table for this system is

	$\text{HSO}_4^-$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{SO}_4^{2-}$
Initial concentration (M)	0.50				~0		0
Change (M)	-x				+x		+x
Equilibrium concentration (M)	$0.50 - x$				x		x

Substituting the equilibrium concentration terms into the  $K_a$  expression gives

**Equation:**

$$K_a = 1.2 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that  $x \ll 0.5$  is made, simplifying and solving the above equation yields

**Equation:**

$$x = 0.077 \text{ M}$$

This value of  $x$  is clearly not significantly less than  $0.50 \text{ M}$ ; rather, it is approximately 15% of the initial concentration:

When we check the assumption, we calculate:

**Equation:**

$$\frac{x}{[\text{HSO}_4^-]_i}$$

**Equation:**

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15 \text{ (15\%)}$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

**Equation:**

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

**Equation:**

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^2$$

Writing the equation in quadratic form gives

**Equation:**

$$x^2 + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to  $x$ . As defined in the ICE table,  $x$  is equal to the hydronium concentration.

**Equation:**

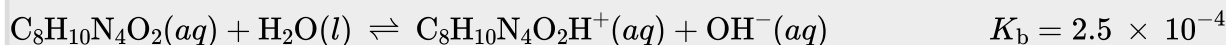
$$x = [\text{H}_3\text{O}^+] = 0.072 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.072) = 1.14$$

### Check Your Learning

Calculate the pH in a 0.010- $M$  solution of caffeine, a weak base:

**Equation:**



**Note:**

**Answer:**

pH 11.16

## Effect of Molecular Structure on Acid-Base Strength

### Binary Acids and Bases

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ . Likewise, for group 16, the order of increasing acid strength is  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ .

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is  $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ ; across the third row, it is  $\text{SiH}_4 < \text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$  (see [link](#)).

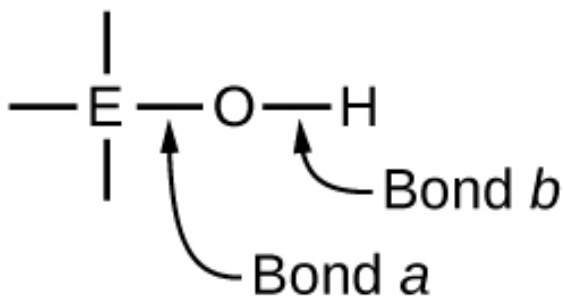


14	15	16	17	
6 <b>CH<sub>4</sub></b> Neither acid nor base	7 <b>NH<sub>3</sub></b> Weak base $K_b = 1.8 \times 10^{-5}$	8 <b>H<sub>2</sub>O</b> Neutral	9 <b>HF</b> Weak acid $K_a = 6.8 \times 10^{-4}$	<div>Increasing acid strength</div> <div>Increasing base strength</div>
14 <b>SiH<sub>4</sub></b> Neither acid nor base	15 <b>PH<sub>3</sub></b> Very weak base $K_b = 4 \times 10^{-28}$	16 <b>H<sub>2</sub>S</b> Weak acid $K_a = 9.5 \times 10^{-8}$	17 <b>HCl</b> Strong acid	
<div>Increasing acid strength</div> <div>Increasing base strength</div>				

The figure shows trends in the strengths of binary acids and bases.

## Ternary Acids and Bases

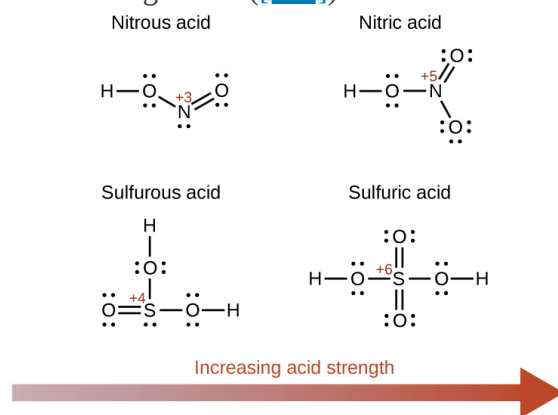
Ternary compounds composed of hydrogen, oxygen, and some third element (“E”) may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula  $O_mE(OH)_n$ . These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid,  $O_2S(OH)_2$ , sulfurous acid,  $OS(OH)_2$ , nitric acid,  $O_2NOH$ , perchloric acid,  $O_3ClOH$ , aluminum hydroxide,  $Al(OH)_3$ , calcium hydroxide,  $Ca(OH)_2$ , and potassium hydroxide,  $KOH$ :



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with  $Ca(OH)_2$  and  $KOH$ . Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic –OH groups that are called **oxyacids**.

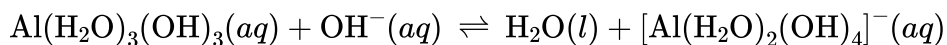
Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid,  $\text{H}_2\text{SO}_4$ , or  $\text{O}_2\text{S}(\text{OH})_2$  (with a sulfur oxidation number of +6), is more acidic than sulfurous acid,  $\text{H}_2\text{SO}_3$ , or  $\text{OS}(\text{OH})_2$  (with a sulfur oxidation number of +4). Likewise nitric acid,  $\text{HNO}_3$ , or  $\text{O}_2\text{NOH}$  (N oxidation number = +5), is more acidic than nitrous acid,  $\text{HNO}_2$ , or  $\text{ONOH}$  (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid ([link](#)).



As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ , is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide,  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ , is converted into the soluble ion,  $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$ , by reaction with hydroxide ion:

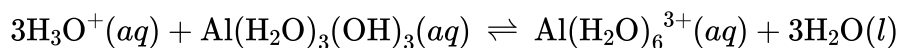
**Equation:**



In this reaction, a proton is transferred from one of the aluminum-bound  $\text{H}_2\text{O}$  molecules to a hydroxide ion in solution. The  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$  compound thus acts as an acid under these

conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  by reaction with hydronium ion:

**Equation:**



In this case, protons are transferred from hydronium ions in solution to  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ , and the compound functions as a base.

## Key Concepts and Summary

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. Water exerts a leveling effect on dissolved acids or bases, reacting completely to generate its characteristic hydronium and hydroxide ions (the strongest acid and base that may exist in water). The strengths of the binary acids increase from left to right across a period of the periodic table ( $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ ), and they increase down a group ( $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ ). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ( $\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$ ). The strengths of oxyacids also increase as the electronegativity of the central element increases [ $\text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4$ ].

## Key Equations

$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_{\text{b}} = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

$$K_{\text{a}} \times K_{\text{b}} = 1.0 \times 10^{-14} = K_{\text{w}}$$

$$\text{Percent ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$$

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:**

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

**Exercise:****Problem:**

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

---

**Solution:**

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms  $\text{OH}^-$ , which causes the solution to be basic.

**Exercise:****Problem:**

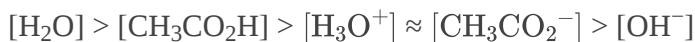
Use this list of important industrial compounds (and [\[link\]](#)) to answer the following questions regarding:  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{CH}_3\text{CO}_2\text{H}$ ,  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HF}$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ .

- (a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
- (b) List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ .
- (c) List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of  $\text{H}_2\text{O}$  and  $\text{OH}^-$ .

**Exercise:****Problem:**

The odor of vinegar is due to the presence of acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

---

**Solution:****Exercise:****Problem:**

Household ammonia is a solution of the weak base  $\text{NH}_3$  in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

**Exercise:**

**Problem:**

Explain why the ionization constant,  $K_a$ , for  $\text{H}_2\text{SO}_4$  is larger than the ionization constant for  $\text{H}_2\text{SO}_3$ .

---

**Solution:**

The oxidation state of the sulfur in  $\text{H}_2\text{SO}_4$  is greater than the oxidation state of the sulfur in  $\text{H}_2\text{SO}_3$ .

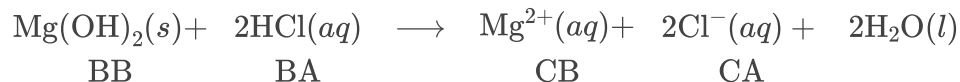
**Exercise:****Problem:**

Explain why the ionization constant,  $K_a$ , for HI is larger than the ionization constant for HF.

**Exercise:****Problem:**

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid  $\text{Mg}(\text{OH})_2$  in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

---

**Solution:****Exercise:****Problem:**

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate,  $\text{Cu}(\text{NO}_3)_2$ , a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of  $\text{HNO}_3$  with  $\text{CuO}$ .

**Exercise:****Problem:**

What is the ionization constant at 25 °C for the weak acid  $\text{CH}_3\text{NH}_3^+$ , the conjugate acid of the weak base  $\text{CH}_3\text{NH}_2$ ,  $K_b = 4.4 \times 10^{-4}$ .

---

**Solution:**

$$K_a = 2.3 \times 10^{-11}$$

**Exercise:**

**Problem:**

What is the ionization constant at 25 °C for the weak acid  $(\text{CH}_3)_2\text{NH}_2^+$ , the conjugate acid of the weak base  $(\text{CH}_3)_2\text{NH}$ ,  $K_b = 5.9 \times 10^{-4}$ ?

**Exercise:****Problem:**

Which base,  $\text{CH}_3\text{NH}_2$  or  $(\text{CH}_3)_2\text{NH}$ , is the stronger base? Which conjugate acid,  $(\text{CH}_3)_2\text{NH}_2^+$  or  $\text{CH}_3\text{NH}_3^+$ , is the stronger acid?

---

**Solution:**

The stronger base or stronger acid is the one with the larger  $K_b$  or  $K_a$ , respectively. In these two examples, they are  $(\text{CH}_3)_2\text{NH}$  and  $\text{CH}_3\text{NH}_3^+$ .

**Exercise:**

**Problem:** Which is the stronger acid,  $\text{NH}_4^+$  or  $\text{HBrO}$ ?

**Exercise:**

**Problem:** Which is the stronger base,  $(\text{CH}_3)_3\text{N}$  or  $\text{H}_2\text{BO}_3^-$ ?

---

**Solution:**

triethylamine

**Exercise:****Problem:**

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a)  $\text{H}_2\text{O}$  or  $\text{HF}$

(b)  $\text{B}(\text{OH})_3$  or  $\text{Al}(\text{OH})_3$

(c)  $\text{HSO}_3^-$  or  $\text{HSO}_4^-$

(d)  $\text{NH}_3$  or  $\text{H}_2\text{S}$

(e)  $\text{H}_2\text{O}$  or  $\text{H}_2\text{Te}$

**Exercise:****Problem:**

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a)  $\text{HSO}_4^-$  or  $\text{HSeO}_4^-$

(b)  $\text{NH}_3$  or  $\text{H}_2\text{O}$

(c)  $\text{PH}_3$  or  $\text{HI}$

(d)  $\text{NH}_3$  or  $\text{PH}_3$

(e)  $\text{H}_2\text{S}$  or  $\text{HBr}$

---

**Solution:**

(a)  $\text{HSO}_4^-$ ; higher electronegativity of the central ion. (b)  $\text{H}_2\text{O}$ ;  $\text{NH}_3$  is a base and water is neutral, or decide on the basis of  $K_a$  values. (c)  $\text{HI}$ ;  $\text{PH}_3$  is weaker than  $\text{HCl}$ ;  $\text{HCl}$  is weaker than  $\text{HI}$ . Thus,  $\text{PH}_3$  is weaker than  $\text{HI}$ . (d)  $\text{PH}_3$ ; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e)  $\text{HBr}$ ; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so  $\text{HBr}$  is the stronger acid.

**Exercise:**

**Problem:**

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity:  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$

(b) basicity:  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{H}^-$ ,  $\text{Cl}^-$

(c) basicity:  $\text{Mg}(\text{OH})_2$ ,  $\text{Si}(\text{OH})_4$ ,  $\text{ClO}_3(\text{OH})$  (Hint: Formula could also be written as  $\text{HClO}_4$ .)

(d) acidity:  $\text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$

**Exercise:**

**Problem:**

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity:  $\text{NaHSO}_3$ ,  $\text{NaHSeO}_3$ ,  $\text{NaHSO}_4$

(b) basicity:  $\text{BrO}_2^-$ ,  $\text{ClO}_2^-$ ,  $\text{IO}_2^-$

(c) acidity:  $\text{HOCl}$ ,  $\text{HOBr}$ ,  $\text{HOI}$

(d) acidity:  $\text{HOCl}$ ,  $\text{HOClO}$ ,  $\text{HOClO}_2$ ,  $\text{HOClO}_3$

(e) basicity:  $\text{NH}_2^-$ ,  $\text{HS}^-$ ,  $\text{HTe}^-$ ,  $\text{PH}_2^-$

(f) basicity:  $\text{BrO}^-$ ,  $\text{BrO}_2^-$ ,  $\text{BrO}_3^-$ ,  $\text{BrO}_4^-$

---

**Solution:**

(a)  $\text{NaHSeO}_3 < \text{NaHSO}_3 < \text{NaHSO}_4$ ; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b)  $\text{ClO}_2^- < \text{BrO}_2^- < \text{IO}_2^-$ ; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c)  $\text{HOI} < \text{HOBr} < \text{HOCl}$ ; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d)  $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$ ; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e)  $\text{HTe}^- < \text{HS}^- \ll \text{PH}_2^- < \text{NH}_2^-$ ;  $\text{PH}_2^-$  and  $\text{NH}_2^-$  are anions of weak bases, so they act as strong bases toward  $\text{H}^+$ .  $\text{HTe}^-$  and  $\text{HS}^-$  are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f)  $\text{BrO}_4^- < \text{BrO}_3^- < \text{BrO}_2^- < \text{BrO}^-$ ; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

**Exercise:****Problem:**

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases,  $\text{F}^-$  or  $\text{CN}^-$ , is the stronger base?

**Exercise:****Problem:**

The active ingredient formed by aspirin in the body is salicylic acid,  $\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})$ . The carboxyl group ( $-\text{CO}_2\text{H}$ ) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-M aqueous solution of  $\text{C}_6\text{H}_4\text{OH}(\text{CO}_2\text{H})$ .

---

**Solution:****Exercise:****Problem:**

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

**Exercise:**



**Problem:**

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid or base?

---

**Solution:**

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of  $\text{H}_3\text{O}^+$ .

**Exercise:****Problem:**

Which of the following will increase the percent of  $\text{NH}_3$  that is converted to the ammonium ion in water?

- (a) addition of  $\text{NaOH}$
  - (b) addition of  $\text{HCl}$
  - (c) addition of  $\text{NH}_4\text{Cl}$
- 

**Solution:**

- (b) The addition of  $\text{HCl}$

**Exercise:****Problem:**

Which of the following will increase the percentage of  $\text{HF}$  that is converted to the fluoride ion in water?

- (a) addition of  $\text{NaOH}$
- (b) addition of  $\text{HCl}$
- (c) addition of  $\text{NaF}$

**Exercise:****Problem:**

What is the effect on the concentrations of  $\text{NO}_2^-$ ,  $\text{HNO}_2$ , and  $\text{OH}^-$  when the following are added to a solution of  $\text{KNO}_2$  in water:

- (a)  $\text{HCl}$
- (b)  $\text{HNO}_2$

(c) NaOH

(d) NaCl

(e) KNO

---

**Solution:**

(a) Adding HCl will add  $\text{H}_3\text{O}^+$  ions, which will then react with the  $\text{OH}^-$  ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of  $\text{HNO}_2$ , and decreasing the concentration of  $\text{NO}_2^-$  ions. (b) Adding  $\text{HNO}_2$  increases the concentration of  $\text{HNO}_2$  and shifts the equilibrium to the left, increasing the concentration of  $\text{NO}_2^-$  ions and decreasing the concentration of  $\text{OH}^-$  ions. (c) Adding NaOH adds  $\text{OH}^-$  ions, which shifts the equilibrium to the left, increasing the concentration of  $\text{NO}_2^-$  ions and decreasing the concentrations of  $\text{HNO}_2$ . (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding  $\text{KNO}_2$  adds  $\text{NO}_2^-$  ions and shifts the equilibrium to the right, increasing the  $\text{HNO}_2$  and  $\text{OH}^-$  ion concentrations.

**Exercise:**

**Problem:**

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

(a) HCl

(b) KF

(c) NaCl

(d) KOH

(e) HF

**Exercise:**

**Problem:**

Why is the hydronium ion concentration in a solution that is 0.10 M in HCl and 0.10 M in  $\text{HCOOH}$  determined by the concentration of HCl?

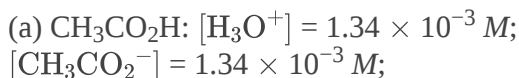
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**Solution:**

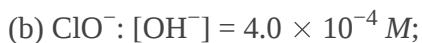
This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the  $\text{HCO}_2\text{H}$  exists primarily as  $\text{HCO}_2\text{H}$  molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the  $\text{HCO}_2\text{H}$  contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the  $[\text{H}_3\text{O}^+]$  produced by the stronger acid.

**Exercise:****Problem:**

From the equilibrium concentrations given, calculate  $K_a$  for each of the weak acids and  $K_b$  for each of the weak bases.

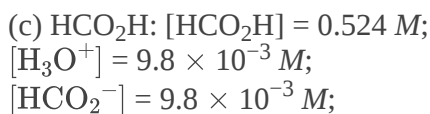


$$[\text{CH}_3\text{CO}_2\text{H}] = 9.866 \times 10^{-2} \text{ M};$$



$$[\text{HClO}] = 2.38 \times 10^{-4} \text{ M};$$

$$[\text{ClO}^-] = 0.273 \text{ M};$$

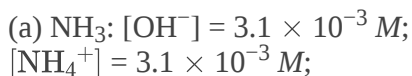


$$[\text{C}_6\text{H}_5\text{NH}_2] = 2.3 \times 10^{-3} \text{ M};$$

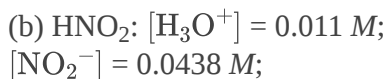
$$[\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$$

**Exercise:****Problem:**

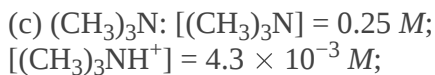
From the equilibrium concentrations given, calculate  $K_a$  for each of the weak acids and  $K_b$  for each of the weak bases.



$$[\text{NH}_3] = 0.533 \text{ M};$$



$$[\text{HNO}_2] = 1.07 \text{ M};$$



$$[\text{OH}^-] = 3.7 \times 10^{-3} \text{ M};$$



$$[\text{NH}_3] = 7.5 \times 10^{-6} \text{ M};$$
$$[\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$$

---

**Solution:**

$$(a) K_b = 1.8 \times 10^{-5}; (b) K_a = 4.5 \times 10^{-4}; (c) K_b = 7.4 \times 10^{-5}; (d)$$
$$K_a = 5.6 \times 10^{-10}$$

**Exercise:**

**Problem:**

Determine  $K_b$  for the nitrite ion,  $\text{NO}_2^-$ . In a 0.10-M solution this base is 0.0015% ionized.

**Exercise:**

**Problem:**

Determine  $K_a$  for hydrogen sulfate ion,  $\text{HSO}_4^-$ . In a 0.10-M solution the acid is 29% ionized.

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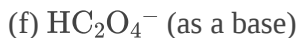
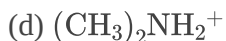
**Solution:**

$$K_a = 1.2 \times 10^{-2}$$

**Exercise:**

**Problem:**

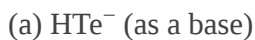
Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:



**Exercise:**

**Problem:**

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:



(c)  $\text{HAsO}_4^{3-}$  (as a base)

(d)  $\text{HO}_2^-$  (as a base)

(e)  $\text{C}_6\text{H}_5\text{NH}_3^+$

(f)  $\text{HSO}_3^-$  (as a base)

---

**Solution:**

(a)  $K_b = 4.3 \times 10^{-12}$  (b)  $K_a = 1.6 \times 10^{-8}$  (c)  $K_b = 5.9 \times 10^{-7}$  (d)  $K_b = 4.2 \times 10^{-3}$   
(e)  $K_b = 2.3 \times 10^{-3}$  (f)  $K_b = 6.3 \times 10^{-13}$

**Exercise:**

**Problem:**

Using the  $K_a$  value of  $1.4 \times 10^{-5}$ , place  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  in the correct location in [\[link\]](#).

**Exercise:**

**Problem:**

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.

(a) 0.0092 M  $\text{HClO}$ , a weak acid

(b) 0.0784 M  $\text{C}_6\text{H}_5\text{NH}_2$ , a weak base

(c) 0.0810 M  $\text{HCN}$ , a weak acid

(d) 0.11 M  $(\text{CH}_3)_3\text{N}$ , a weak base

(e) 0.120 M  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  a weak acid,  $K_a = 1.6 \times 10^{-7}$

---

**Solution:**

$$(a) \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(x)(x)}{(0.0092-x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$$

Solving for  $x$  gives  $1.63 \times 10^{-5} \text{ M}$ . This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{ClO}^-] = 1.63 \times 10^{-5} \text{ M}$$

$$[\text{HClO}] = 0.0092 \text{ M}$$

$$[\text{OH}^-] = 6.1 \times 10^{-10} \text{ M};$$

$$(b) \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{(x)(x)}{(0.0784-x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$$

Solving for  $x$  gives  $5.81 \times 10^{-6} \text{ M}$ . This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{CH}_3\text{CO}_2^-] = [\text{OH}^-] = 5.8 \times 10^{-6} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.0784$$

$$[\text{H}_3\text{O}^+] = 1.7 \times 10^{-9} \text{ M};$$

$$(c) \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(x)}{(0.0810-x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$$

Solving for  $x$  gives  $6.30 \times 10^{-6} \text{ M}$ . This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{H}_3\text{O}^+] = [\text{CN}^-] = 6.3 \times 10^{-6} \text{ M}$$

$$[\text{HCN}] = 0.0810 \text{ M}$$

$$[\text{OH}^-] = 1.6 \times 10^{-9} \text{ M};$$

$$(d) \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{(0.11-x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$$

Solving for  $x$  gives  $2.63 \times 10^{-3} \text{ M}$ . This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[(\text{CH}_3)_3\text{NH}^+] = [\text{OH}^-] = 2.6 \times 10^{-3} \text{ M}$$

$$[(\text{CH}_3)_3\text{N}] = 0.11 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 3.8 \times 10^{-12} \text{ M};$$

$$(e) \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{2+}]} = \frac{(x)(x)}{(0.120-x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

Solving for  $x$  gives  $1.39 \times 10^{-4} \text{ M}$ . This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^+] = [\text{H}_3\text{O}^+] = 1.4 \times 10^{-4} \text{ M}$$

$$[\text{Fe}(\text{H}_2\text{O})_6^{2+}] = 0.120 \text{ M}$$

$$[\text{OH}^-] = 7.2 \times 10^{-11} \text{ M}$$

### Exercise:

#### Problem:

Propionic acid,  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$  ( $K_a = 1.34 \times 10^{-5}$ ), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-M solution of  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ ?

### Exercise:

#### Problem:

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is  $1.007 \text{ g/cm}^3$ , what is the pH?

#### Solution:

$$\text{pH} = 2.41$$

### Exercise:

#### Problem:

The ionization constant of lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$ , an acid found in the blood after strenuous exercise, is  $1.36 \times 10^{-4}$ . If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

### Exercise:

**Problem:**

Nicotine,  $\text{C}_{10}\text{H}_{14}\text{N}_2$ , is a base that will accept two protons ( $K_{b1} = 7 \times 10^{-7}$ ,  $K_{b2} = 1.4 \times 10^{-11}$ ). What is the concentration of each species present in a 0.050- $M$  solution of nicotine?

---

**Solution:**

$[\text{C}_{10}\text{H}_{14}\text{N}_2] = 0.049\text{ M}$ ;  $[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+] = 1.9 \times 10^{-4}\text{ M}$ ;  $[\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}_2^{2+}] = 1.4 \times 10^{-11}\text{ M}$ ;  
 $[\text{OH}^-] = 1.9 \times 10^{-4}\text{ M}$ ;  $[\text{H}_3\text{O}^+] = 5.3 \times 10^{-11}\text{ M}$

**Exercise:**

**Problem:** The pH of a 0.23- $M$  solution of HF is 1.92. Determine  $K_a$  for HF from these data.

**Exercise:****Problem:**

The pH of a 0.15- $M$  solution of  $\text{HSO}_4^-$  is 1.43. Determine  $K_a$  for  $\text{HSO}_4^-$  from these data.

---

**Solution:**

$$K_a = 1.2 \times 10^{-2}$$

**Exercise:****Problem:**

The pH of a 0.10- $M$  solution of caffeine is 11.70. Determine  $K_b$  for caffeine from these data:  
 $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+(aq) + \text{OH}^-(aq)$

**Exercise:****Problem:**

The pH of a solution of household ammonia, a 0.950  $M$  solution of  $\text{NH}_3$ , is 11.612. Determine  $K_b$  for  $\text{NH}_3$  from these data.

---

**Solution:**

$$K_b = 1.77 \times 10^{-5}$$

**Glossary**

acid ionization constant ( $K_a$ )  
equilibrium constant for an acid ionization reaction

base ionization constant ( $K_b$ )  
equilibrium constant for a base ionization reaction

leveling effect

observation that acid-base strength of solutes in a given solvent is limited to that of the solvent's characteristic acid and base species (in water, hydronium and hydroxide ions, respectively)

oxyacid

ternary compound with acidic properties, molecules of which contain a central nonmetallic atom bonded to one or more O atoms, at least one of which is bonded to an ionizable H atom

percent ionization

ratio of the concentration of ionized acid to initial acid concentration expressed as a percentage



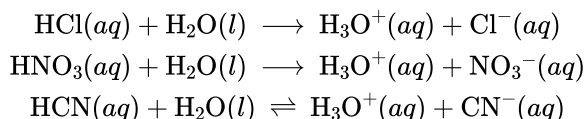
## Polyprotic Acids

By the end of this section, you will be able to:

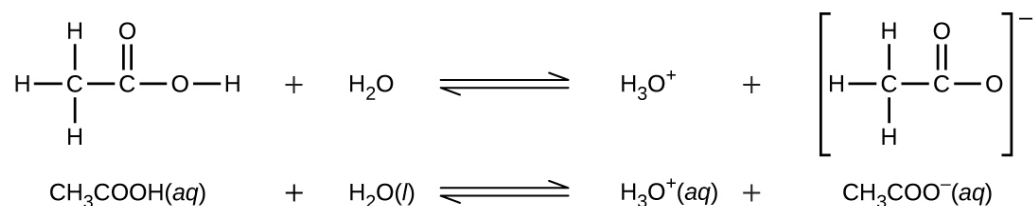
- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO<sub>3</sub>, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

**Equation:**



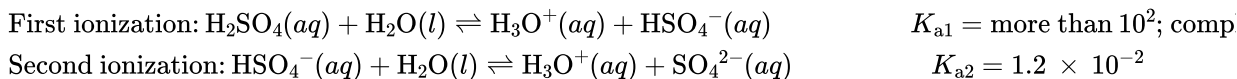
Even though it contains four hydrogen atoms, acetic acid, CH<sub>3</sub>CO<sub>2</sub>H, is also monoprotic because only the hydrogen atom from the carboxyl group (COOH) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

**Diprotic acids** contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

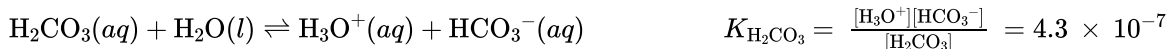
**Equation:**



This **stepwise ionization** process occurs for all polyprotic acids. Carbonic acid, H<sub>2</sub>CO<sub>3</sub>, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

**Equation:**

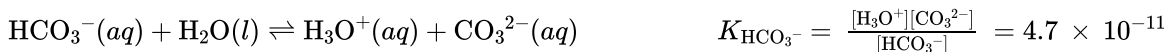
First ionization:



The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

**Equation:**

Second ionization:



$K_{\text{H}_2\text{CO}_3}$  is larger than  $K_{\text{HCO}_3^-}$  by a factor of  $10^4$ , so  $\text{H}_2\text{CO}_3$  is the dominant producer of hydronium ion in the solution. This means that little of the  $\text{HCO}_3^-$  formed by the ionization of  $\text{H}_2\text{CO}_3$  ionizes to give hydronium ions (and carbonate ions), and the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{HCO}_3^-$  are practically equal in a pure aqueous solution of  $\text{H}_2\text{CO}_3$ .

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This approach is demonstrated in the following example exercise.

**Example:**

**Ionization of a Diprotic Acid**

“Carbonated water” contains a palatable amount of dissolved carbon dioxide. The solution is acidic because  $\text{CO}_2$  reacts with water to form carbonic acid,  $\text{H}_2\text{CO}_3$ . What are  $[\text{H}_3\text{O}^+]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$  in a saturated solution of  $\text{CO}_2$  with an initial  $[\text{H}_2\text{CO}_3] = 0.033\text{ M}$ ?

**Equation:**



**Equation:**



**Solution**

As indicated by the ionization constants,  $\text{H}_2\text{CO}_3$  is a much stronger acid than  $\text{HCO}_3^-$ , so the stepwise ionization reactions may be treated separately.

The first ionization reaction is

**Equation:**



Using provided information, an ICE table for this first step is prepared:

	$\text{H}_2\text{CO}_3$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{HCO}_3^-$
Initial concentration (M)	0.033				~0		0
Change (M)	-x				+x		+x
Equilibrium concentration (M)	$0.033 - x$				x		x

Substituting the equilibrium concentrations into the equilibrium equation gives

**Equation:**

$$K_{\text{H}_2\text{CO}_3} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming  $x \ll 0.033$  and solving the simplified equation yields

**Equation:**

$$x = 1.2 \times 10^{-4}$$

The ICE table defined  $x$  as equal to the bicarbonate ion molarity and the hydronium ion molarity:

**Equation:**

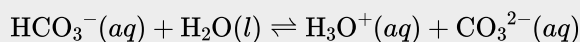
$$[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$$

**Equation:**

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 1.2 \times 10^{-4} \text{ M}$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

**Equation:**



**Equation:**

$$K_{\text{HCO}_3^-} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(1.2 \times 10^{-4})[\text{CO}_3^{2-}]}{1.2 \times 10^{-4}}$$

**Equation:**

$$[\text{CO}_3^{2-}] = \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11} \text{ M}$$

To summarize: at equilibrium  $[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$ ;  $[\text{H}_3\text{O}^+] = 1.2 \times 10^{-4}$ ;  $[\text{HCO}_3^-] = 1.2 \times 10^{-4} \text{ M}$ ;  $[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M}$ .

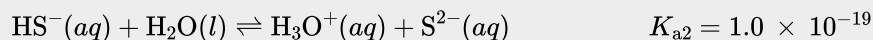
#### Check Your Learning

The concentration of  $\text{H}_2\text{S}$  in a saturated aqueous solution at room temperature is approximately  $0.1 \text{ M}$ . Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{HS}^-]$ , and  $[\text{S}^{2-}]$  in the solution:

**Equation:**



**Equation:**



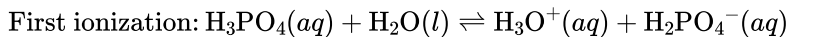
**Note:**

**Answer:**

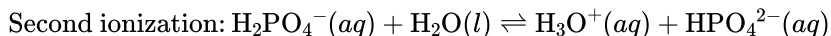
$$[\text{H}_2\text{S}] = 0.1 \text{ M}; [\text{H}_3\text{O}^+] = [\text{HS}^-] = 0.000094 \text{ M}; [\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$$

A **triprotic acid** is an acid that has three ionizable H atoms. Phosphoric acid is one example:

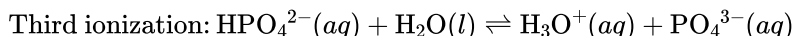
**Equation:**



$$K_{a1} = 7.5 \times 10^{-3}$$



$$K_{a2} = 6.2 \times 10^{-8}$$



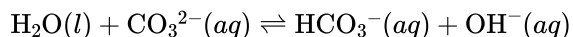
$$K_{a3} = 4.2 \times 10^{-13}$$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about  $10^5$  to  $10^6$ .

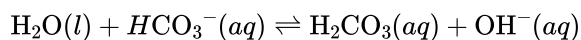
This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of  $\text{H}_3\text{PO}_4$  complicated. However, because the successive ionization constants differ by a factor of  $10^5$  to  $10^6$ , large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a **diprotic base**, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

**Equation:**



$$K_{b1} = 2.1 \times 10^{-4}$$



$$K_{b2} = 2.3 \times 10^{-8}$$

## Key Concepts and Summary

An acid that contains more than one ionizable proton is a polyprotic acid. These acids undergo stepwise ionization reactions involving the transfer of single protons. The ionization constants for polyprotic acids decrease with each subsequent step; these decreases typically are large enough to permit simple equilibrium calculations that treat each step separately.

## Chemistry End of Chapter Exercises

**Exercise:**

**Problem:**

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-M solution of  $\text{H}_2\text{CO}_3$ , a diprotic acid:  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ ,  $[\text{H}_2\text{CO}_3]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ ? No calculations are needed to answer this question.

---

**Solution:**

$[\text{H}_3\text{O}^+]$  and  $[\text{HCO}_3^-]$  are practically equal

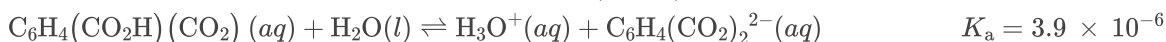
**Exercise:**

**Problem:** Calculate the concentration of each species present in a 0.050-M solution of  $\text{H}_2\text{S}$ .

**Exercise:**

**Problem:**

Calculate the concentration of each species present in a 0.010-M solution of phthalic acid,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ .

**Solution:**

$[\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2] 7.2 \times 10^{-3} \text{ M}$ ,  $[\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2)^-] = [\text{H}_3\text{O}^+] 2.8 \times 10^{-3} \text{ M}$ ,  $[\text{C}_6\text{H}_4(\text{CO}_2)_2^{2-}] 3.9 \times 10^{-6} \text{ M}$ ,  $[\text{OH}^-] 3.6 \times 10^{-12} \text{ M}$

**Exercise:****Problem:**

Salicylic acid,  $\text{HOC}_6\text{H}_4\text{CO}_2\text{H}$ , and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with  $K_a = 1.0 \times 10^{-3}$  for the  $-\text{CO}_2\text{H}$  group and  $4.2 \times 10^{-13}$  for the  $-\text{OH}$  group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid,  $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ . The  $-\text{CO}_2\text{H}$  functional group is still present, but its acidity is reduced,  $K_a = 3.0 \times 10^{-4}$ . What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

**Exercise:**

**Problem:** The ion  $\text{HTe}^-$  is an amphiprotic species; it can act as either an acid or a base.

(a) What is  $K_a$  for the acid reaction of  $\text{HTe}^-$  with  $\text{H}_2\text{O}$ ?

(b) What is  $K_b$  for the reaction in which  $\text{HTe}^-$  functions as a base in water?

(c) Demonstrate whether or not the second ionization of  $\text{H}_2\text{Te}$  can be neglected in the calculation of  $[\text{HTe}^-]$  in a 0.10 M solution of  $\text{H}_2\text{Te}$ .

**Solution:**

(a)  $K_{a2} = 1.5 \times 10^{-11}$ ;

(b)  $K_b = 4.3 \times 10^{-12}$ ;

(c)  $\frac{[\text{Te}^{2-}][\text{H}_3\text{O}^+]}{[\text{HTe}^-]} = \frac{(x)(0.0141+x)}{(0.0141-x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.5 \times 10^{-11}$

Solving for  $x$  gives  $1.5 \times 10^{-11} \text{ M}$ . Therefore, compared with 0.014 M, this value is negligible ( $1.1 \times 10^{-7}\%$ ).

**Glossary**

diprotic acid

acid containing two ionizable hydrogen atoms per molecule

diprotic base

base capable of accepting two protons

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which a polyprotic acid is ionized by losing protons sequentially

triprotic acid

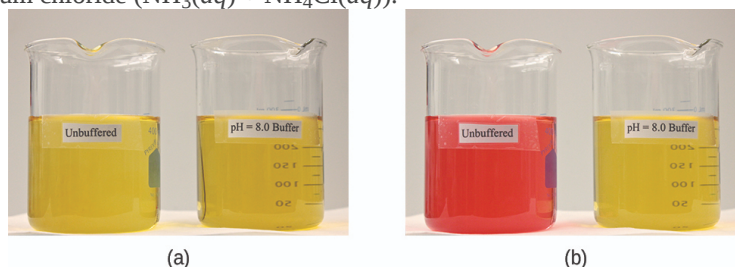
acid that contains three ionizable hydrogen atoms per molecule

## Buffers

By the end of this section, you will be able to:

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added ([link](#)). A solution of acetic acid and sodium acetate ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ ) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ( $\text{NH}_3(\text{aq}) + \text{NH}_4\text{Cl}(\text{aq})$ ).



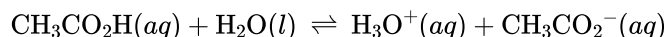
(a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b)

After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

## How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, adding strong base to this solution will neutralize hydronium ion and shift the acetic acid ionization equilibrium to the right, partially restoring the decreased  $\text{H}_3\text{O}^+$  concentration:

**Equation:**

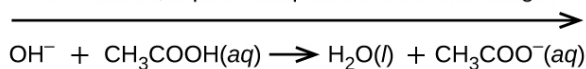
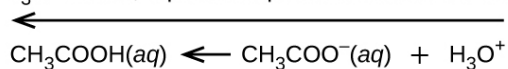


Likewise, adding strong acid to this buffer solution will neutralize acetate ion, shifting the above ionization equilibrium right and returning  $[\text{H}_3\text{O}^+]$  to near its original value. [link](#) provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.



$\text{H}_3\text{O}^+$  added, equilibrium position shifts to the left

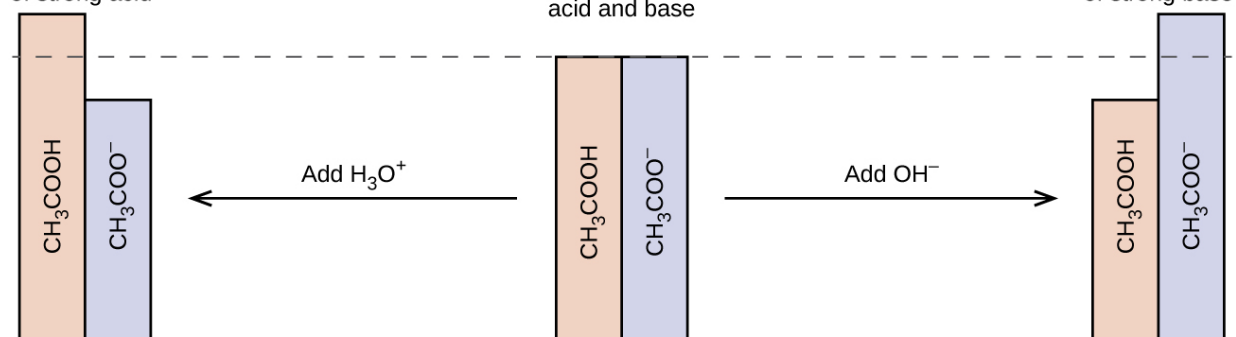
$\text{OH}^-$  added, equilibrium position shifts to the right



Buffer solution  
after addition  
of strong acid

Buffer solution  
equimolar in  
acid and base

Buffer solution  
after addition  
of strong base



Buffering action in a mixture of acetic acid and acetate salt.

### Example:

#### pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

- Calculate the pH of an acetate buffer that is a mixture with 0.10 M acetic acid and 0.10 M sodium acetate.
- Calculate the pH after 1.0 mL of 0.10 NaOH is added to 100 mL of this buffer.
- For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

#### Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

	$\text{CH}_3\text{CO}_2\text{H}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{CH}_3\text{CO}_2^-$
Initial concentration (M)	0.10				~0		0.10
Change (M)	-x				+x		+x
Equilibrium concentration (M)	0.10 - x				x		0.10 + x

Substituting the equilibrium concentration terms into the  $K_a$  expression, assuming  $x \ll 0.10$ , and solving the simplified equation for x yields

#### Equation:

$$x = 1.8 \times 10^{-5} \text{ M}$$



**Equation:**

$$[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5} M$$

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.8 \times 10^{-5})$$

**Equation:**

$$= 4.74$$

(b) Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer.

Adding strong acid will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

**Equation:**

$$0.0010 \cancel{\text{L}} \times \left( \frac{0.10 \text{ mol NaOH}}{1 \cancel{\text{L}}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$$

The initial molar amount of acetic acid is

**Equation:**

$$0.100 \cancel{\text{L}} \times \left( \frac{0.100 \text{ mol CH}_3\text{CO}_2\text{H}}{1 \cancel{\text{L}}} \right) = 1.00 \times 10^{-2} \text{ mol CH}_3\text{CO}_2\text{H}$$

The amount of acetic acid remaining after some is neutralized by the added base is

**Equation:**

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol CH}_3\text{CO}_2\text{H}$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

**Equation:**

$$(1.0 \times 10^{-2}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2} \text{ mol NaCH}_3\text{CO}_2$$

Compute molar concentrations for the two buffer components:

**Equation:**

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 M$$

**Equation:**

$$[\text{NaCH}_3\text{CO}_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 M$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydronium ion initially present in the solution is

**Equation:**

$$[\text{H}_3\text{O}^+] = 10^{-4.74} = 1.8 \times 10^{-5} M$$

**Equation:**

$$\text{mol H}_3\text{O}^+ = (0.100 \text{ L})(1.8 \times 10^{-5} \text{ M}) = 1.8 \times 10^{-6} \text{ mol H}_3\text{O}^+$$

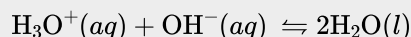
The amount of hydroxide ion added to the solution is

**Equation:**

$$\text{mol OH}^- = (0.0010 \text{ L})(0.10 \text{ M}) = 1.0 \times 10^{-4} \text{ mol OH}^-$$

The added hydroxide will neutralize hydronium ion via the reaction

**Equation:**



The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

**Equation:**

$$1.0 \times 10^{-4} \text{ mol} - 1.8 \times 10^{-6} \text{ mol} = 9.8 \times 10^{-5} \text{ mol OH}^-$$

corresponding to a hydroxide molarity of

**Equation:**

$$9.8 \times 10^{-5} \text{ mol OH}^- / 0.101 \text{ L} = 9.7 \times 10^{-4} \text{ M}$$

The pH of the solution is then calculated to be

**Equation:**

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - -\log(9.7 \times 10^{-4}) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

### Check Your Learning

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a  $1.8 \times 10^{-5} \text{ M}$  HCl solution from 4.74 to 3.00.

**Note:**

**Answer:**

Initial pH of  $1.8 \times 10^{-5} \text{ M}$  HCl;  $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of  $\text{H}_3\text{O}^+$  in 100 mL  $1.8 \times 10^{-5} \text{ M}$  HCl;  $1.8 \times 10^{-5} \text{ moles/L} \times 0.100 \text{ L} = 1.8 \times 10^{-6}$

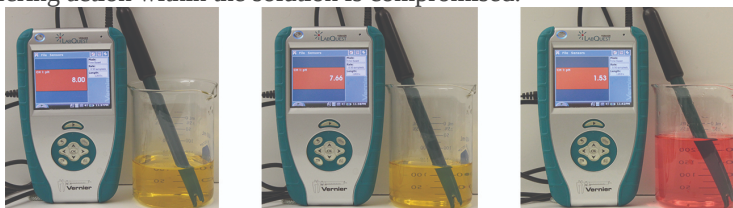
Moles of  $\text{H}_3\text{O}^+$  added by addition of 1.0 mL of 0.10 M HCl:  $0.10 \text{ moles/L} \times 0.0010 \text{ L} = 1.0 \times 10^{-4} \text{ moles}$ ; final pH after addition of 1.0 mL of 0.10 M HCl:

**Equation:**

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} \text{ mol} + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

## Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant ([link](#)). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.



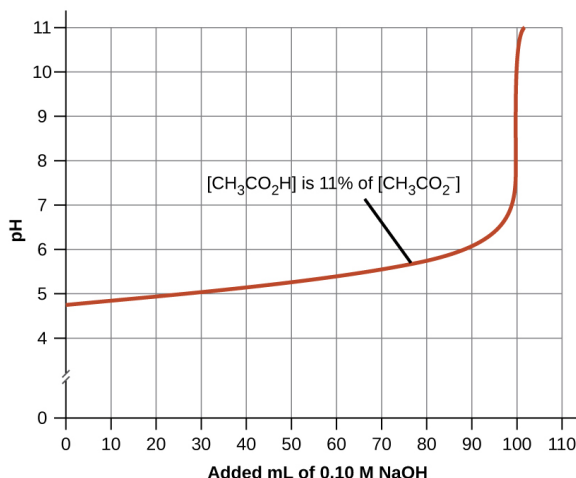
The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

## Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. [link](#) shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

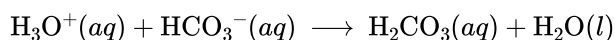


Change in pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially,  $[\text{CH}_3\text{CO}_2\text{H}] = 0.10\text{ M}$  and  $[\text{CH}_3\text{CO}_2^-] = 0.10\text{ M}$ . Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

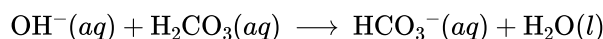
Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid,  $\text{H}_2\text{CO}_3$ , and the bicarbonate ion,  $\text{HCO}_3^-$ . When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

**Equation:**



An added hydroxide ion is removed by the reaction:

**Equation:**



The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair ( $\text{H}_3\text{O}^+$  is converted to  $\text{H}_2\text{CO}_3$  and  $\text{OH}^-$  is converted to  $\text{HCO}_3^-$ ). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

### The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

**Equation:**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Rearranging to solve for  $[\text{H}_3\text{O}^+]$  yields:

**Equation:**

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

Taking the negative logarithm of both sides of this equation gives

**Equation:**

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]},$$

which can be written as

**Equation:**

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

where  $\text{p}K_a$  is the negative of the logarithm of the ionization constant of the weak acid ( $\text{p}K_a = -\log K_a$ ). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the “x is small” assumption must be valid to use this equation.

**Note:**

**Lawrence Joseph Henderson and Karl Albert Hasselbalch**

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

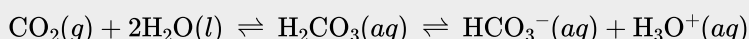
In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson’s equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

**Note:**

**Medicine: The Buffer System in Blood**

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

**Equation:**



The concentration of carbonic acid,  $\text{H}_2\text{CO}_3$  is approximately 0.0012 M, and the concentration of the hydrogen carbonate ion,  $\text{HCO}_3^-$ , is around 0.024 M. Using the Henderson-Hasselbalch equation and the  $\text{p}K_a$  of carbonic acid at body temperature, we can calculate the pH of blood:

**Equation:**

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.4 + \log \frac{0.024}{0.0012} = 7.7$$

The fact that the  $\text{H}_2\text{CO}_3$  concentration is significantly lower than that of the  $\text{HCO}_3^-$  ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the  $\text{HCO}_3^-$  ion, producing  $\text{H}_2\text{CO}_3$ . An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the

regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes  $\text{CO}_2$  from the blood through the lungs driving the equilibrium reaction such that  $[\text{H}_3\text{O}^+]$  is lowered. If the blood is too alkaline, a lower breath rate increases  $\text{CO}_2$  concentration in the blood, driving the equilibrium reaction the other way, increasing  $[\text{H}^+]$  and restoring an appropriate pH.

**Note:**

View [information](#) on the buffer system encountered in natural waters.

## Key Concepts and Summary

Solutions that contain appreciable amounts of a weak conjugate acid-base pair are called buffers. A buffered solution will experience only slight changes in pH when small amounts of acid or base are added. Addition of large amounts of acid or base can exceed the buffer capacity, consuming most of one conjugate partner and preventing further buffering action.

## Key Equations

$$\text{p}K_{\text{a}} = -\log K_{\text{a}}$$

$$\text{p}K_{\text{b}} = -\log K_{\text{b}}$$

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

**Exercise:**

**Problem:**

Explain why a buffer can be prepared from a mixture of  $\text{NH}_4\text{Cl}$  and  $\text{NaOH}$  but not from  $\text{NH}_3$  and  $\text{NaOH}$ .

**Exercise:**

**Problem:**

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid  $\text{H}_3\text{PO}_4$  and a salt of its conjugate base  $\text{NaH}_2\text{PO}_4$ .

**Solution:**

Excess  $\text{H}_3\text{O}^+$  is removed primarily by the reaction:  $\text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}) \longrightarrow \text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Excess base is removed by the reaction:  $\text{OH}^-(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}) \longrightarrow \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

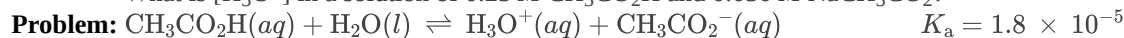
**Exercise:**

**Problem:**

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base  $\text{NH}_3$  and a salt of its conjugate acid  $\text{NH}_4\text{Cl}$ .

**Exercise:**

What is  $[\text{H}_3\text{O}^+]$  in a solution of 0.25 M  $\text{CH}_3\text{CO}_2\text{H}$  and 0.030 M  $\text{NaCH}_3\text{CO}_2$ ?

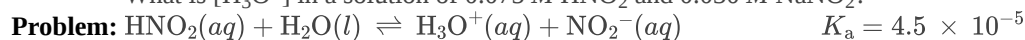


**Solution:**

$$[\text{H}_3\text{O}^+] = 1.5 \times 10^{-4} \text{ M}$$

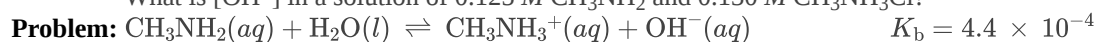
**Exercise:**

What is  $[\text{H}_3\text{O}^+]$  in a solution of 0.075 M  $\text{HNO}_2$  and 0.030 M  $\text{NaNO}_2$ ?



**Exercise:**

What is  $[\text{OH}^-]$  in a solution of 0.125 M  $\text{CH}_3\text{NH}_2$  and 0.130 M  $\text{CH}_3\text{NH}_3\text{Cl}$ ?

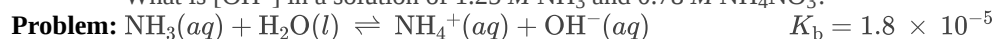


**Solution:**

$$[\text{OH}^-] = 4.2 \times 10^{-4} \text{ M}$$

**Exercise:**

What is  $[\text{OH}^-]$  in a solution of 1.25 M  $\text{NH}_3$  and 0.78 M  $\text{NH}_4\text{NO}_3$ ?



**Exercise:**

**Problem:**

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

- (a)  $\text{HCl}$
  - (b)  $\text{KCH}_3\text{CO}_2$
  - (c)  $\text{NaCl}$
  - (d)  $\text{KOH}$
  - (e)  $\text{CH}_3\text{CO}_2\text{H}$
- 

**Solution:**

(a) The added  $\text{HCl}$  will increase the concentration of  $\text{H}_3\text{O}^+$  slightly, which will react with  $\text{CH}_3\text{CO}_2^-$  and produce  $\text{CH}_3\text{CO}_2\text{H}$  in the process. Thus,  $[\text{CH}_3\text{CO}_2^-]$  decreases and  $[\text{CH}_3\text{CO}_2\text{H}]$  increases. (b) The added  $\text{KCH}_3\text{CO}_2$  will increase the concentration of  $[\text{CH}_3\text{CO}_2^-]$  which will react with  $\text{H}_3\text{O}^+$  and produce  $\text{CH}_3\text{CO}_2\text{H}$  in the process. Thus,  $[\text{H}_3\text{O}^+]$  decreases slightly and  $[\text{CH}_3\text{CO}_2\text{H}]$  increases. (c) The added  $\text{NaCl}$  will have no effect on the concentration of the ions. (d) The added  $\text{KOH}$  will produce  $\text{OH}^-$  ions, which will react with the  $\text{H}_3\text{O}^+$ , thus reducing  $[\text{H}_3\text{O}^+]$ . Some additional  $\text{CH}_3\text{CO}_2\text{H}$  will dissociate, producing  $[\text{CH}_3\text{CO}_2^-]$  ions in the process. Thus,  $[\text{CH}_3\text{CO}_2\text{H}]$  decreases slightly and  $[\text{CH}_3\text{CO}_2^-]$  increases. (e) The added  $\text{CH}_3\text{CO}_2\text{H}$  will increase its concentration, causing more of it to dissociate and producing more  $[\text{CH}_3\text{CO}_2^-]$  and  $\text{H}_3\text{O}^+$  in the process. Thus,  $[\text{H}_3\text{O}^+]$  increases slightly and  $[\text{CH}_3\text{CO}_2^-]$  increases.

**Exercise:**

**Problem:**

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

- (a) KI
- (b)  $\text{NH}_3$
- (c) HI
- (d) NaOH
- (e)  $\text{NH}_4\text{Cl}$

**Exercise:****Problem:**

What will be the pH of a buffer solution prepared from 0.20 mol  $\text{NH}_3$ , 0.40 mol  $\text{NH}_4\text{NO}_3$ , and just enough water to give 1.00 L of solution?

---

**Solution:**

pH = 8.95

**Exercise:****Problem:**

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of  $\text{KH}_2\text{PO}_4$ , and enough water to make 0.500 L of solution.

**Exercise:****Problem:**

How much solid  $\text{NaCH}_3\text{CO}_2 \cdot 3\text{H}_2\text{O}$  must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

---

**Solution:**

37 g (0.27 mol)

**Exercise:****Problem:**

What mass of  $\text{NH}_4\text{Cl}$  must be added to 0.750 L of a 0.100-*M* solution of  $\text{NH}_3$  to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

**Exercise:****Problem:**

A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use  $1.80 \times 10^{-5}$  as  $K_a$  for acetic acid.

- (a) What is the pH of the solution?
- (b) Is the solution acidic or basic?



(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

---

**Solution:**

(a) pH = 5.222; (b) The solution is acidic. (c) pH = 5.221

**Exercise:**

**Problem:** A 5.36-g sample of NH<sub>4</sub>Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.

(a) What is the pH of this buffer solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

**Glossary**

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of appreciable amounts of a weak acid-base pair the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

logarithmic version of the acid ionization constant expression, conveniently formatted for calculating the pH of buffer solutions

## Acid-Base Titrations

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

## Titration Curves

A **titration curve** is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the computation of pH for a titration solution after additions of several specified titrant volumes. The first example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH. The second example addresses a weak acid titration requiring equilibrium calculations.

### Example:

#### Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M of a strong base NaOH (the titration curve is shown in [\[link\]](#)). Calculate the pH at these volumes of added base solution:

- (a) 0.00 mL
- (b) 12.50 mL
- (c) 25.00 mL
- (d) 37.50 mL

#### Solution

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 M. The pH of the solution is then

#### Equation:

$$\text{pH} = -\log (0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the initial amount and then dividing by the solution volume:

#### Equation:

$$[\text{H}_3\text{O}^+] = \frac{n(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100 \text{ M} \times 12.50 \text{ mL}}{25.00 \text{ mL} + 12.50 \text{ mL}} = 0.0333 \text{ M}$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

**Equation:**

$$n(\text{OH}^-)_0 > n(\text{H}^+)_0$$

**Equation:**

$$[\text{OH}^-] = \frac{n(\text{OH}^-)}{V} = \frac{0.100 \text{ M} \times 37.50 \text{ mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL} + 37.50 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log([\text{OH}^-]) = 14 + \log(0.0200) = 12.30$$

### Check Your Learning

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 M  $\text{HNO}_3(aq)$  and 0.200 M NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

**Note:**

**Answer:**

0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

### Example:

#### Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 M  $\text{CH}_3\text{CO}_2\text{H}$  with 0.100 M NaOH. The reaction can be represented as:

**Equation:**



Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

- (a) 0.00 mL
- (b) 25.00 mL
- (c) 12.50 mL

(d) 37.50 mL

**Solution**

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} \approx \frac{[\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{CO}_2\text{H}]_0}, \text{ and}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times [\text{CH}_3\text{CO}_2\text{H}]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

**Equation:**

$$\text{pH} = -\log(1.3 \times 10^{-3}) = 2.87$$

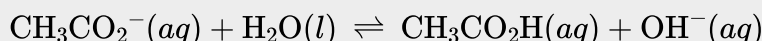
(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

**Equation:**

$$\frac{0.00250 \text{ mol}}{0.0500 \text{ L}} = 0.0500 \text{ MCH}_3\text{CO}_2^-$$

Base ionization of acetate is represented by the equation

**Equation:**



**Equation:**

$$K_b = \frac{[\text{H}^+][\text{OH}^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming  $x \ll 0.0500$ , the pH may be calculated via the usual ICE approach:  $K_b = \frac{x^2}{0.0500 \text{ M}}$

**Equation:**

$$x = [\text{OH}^-] = 5.3 \times 10^{-6}$$

**Equation:**

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28$$

**Equation:**

$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

**Equation:**

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{Base}]}{[\text{Acid}]} = -\log(K_{\text{a}}) + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = -\log(1.8 \times 10^{-5}) + \log(1)$$

**Equation:**

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

(pH = pK<sub>a</sub> at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

**Equation:**

$$[\text{OH}^-] = \frac{(0.003750 \text{ mol} - 0.00250 \text{ mol})}{0.06250 \text{ L}} = 2.00 \times 10^{-2} \text{ M}$$

**Equation:**

$$\text{pOH} = -\log(2.00 \times 10^{-2}) = 1.70, \text{ and } \text{pH} = 14.00 - 1.70 = 12.30$$

**Check Your Learning**

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 M HCOOH(aq) (formic acid) and 0.200 M NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

**Note:****Answer:**

0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Performing additional calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in [\[link\]](#) and plotted as titration curves in [\[link\]](#). A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH

pre-equivalence point (0 mL < V < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction

product, its conjugate base

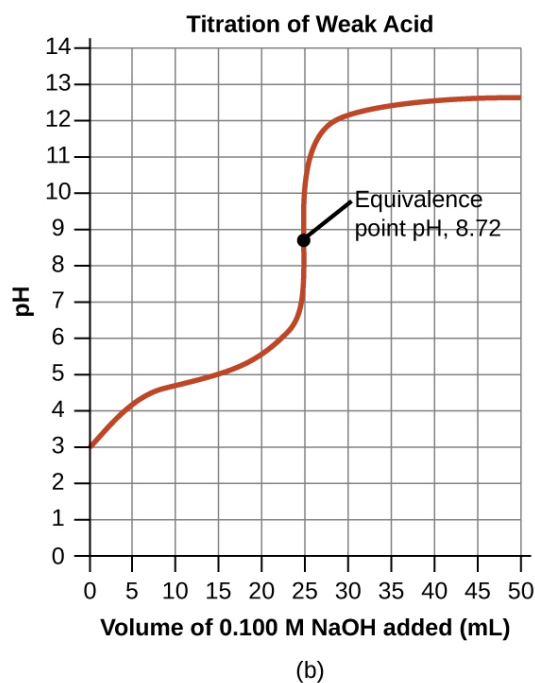
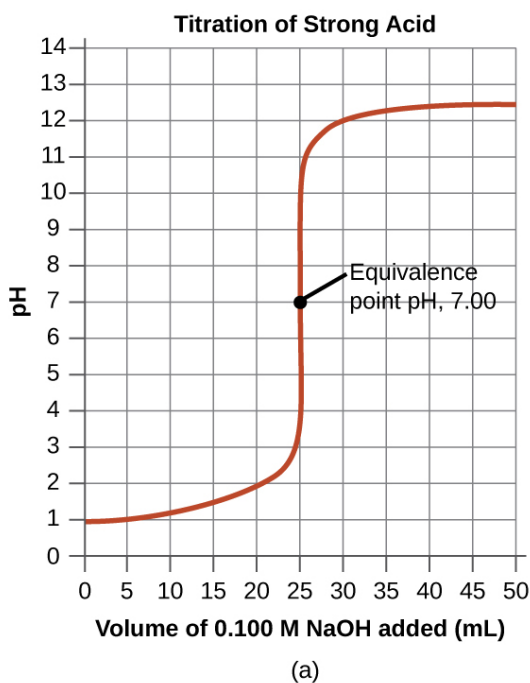
equivalence point ( $V = 25\text{ mL}$ ): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid

postequivalence point ( $V > 25\text{ mL}$ ): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

pH Values in the Titrations of a Strong Acid and of a Weak Acid			
Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl <sup>[footnote]</sup> Titration of 25.00 mL of 0.100 M HCl (0.00250 mol of HCl) with 0.100 M NaOH.	pH Values 0.100 M CH <sub>3</sub> CO <sub>2</sub> H <sup>[footnote]</sup> Titration of 25.00 mL of 0.100 M CH <sub>3</sub> CO <sub>2</sub> H (0.00250 mol of CH <sub>3</sub> CO <sub>2</sub> H) with 0.100 M NaOH.
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00

### pH Values in the Titrations of a Strong Acid and of a Weak Acid

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl <sup>[footnote]</sup> Titration of 25.00 mL of 0.100 M HCl (0.00250 mol of HCl) with 0.100 M NaOH.	pH Values 0.100 M CH <sub>3</sub> CO <sub>2</sub> H <sup>[footnote]</sup> Titration of 25.00 mL of 0.100 M CH <sub>3</sub> CO <sub>2</sub> H (0.00250 mol of CH <sub>3</sub> CO <sub>2</sub> H) with 0.100 M NaOH.
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52



(a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the

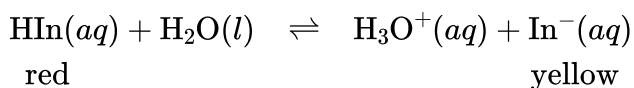
titration of 25.00 mL of 0.100 M acetic acid (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

## Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than  $5.0 \times 10^{-9} M$  ( $pH < 8.3$ ). In more basic solutions where the hydronium ion concentration is less than  $5.0 \times 10^{-9} M$  ( $pH > 8.3$ ), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

**Equation:**



**Equation:**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange,  $\text{In}^-$ , is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Châtelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species  $\text{In}^-$  and HIn. If most of the indicator (typically about 60–90% or more) is present as  $\text{In}^-$ , the perceived color of the solution is yellow. If most is present as HIn, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

**Equation:**

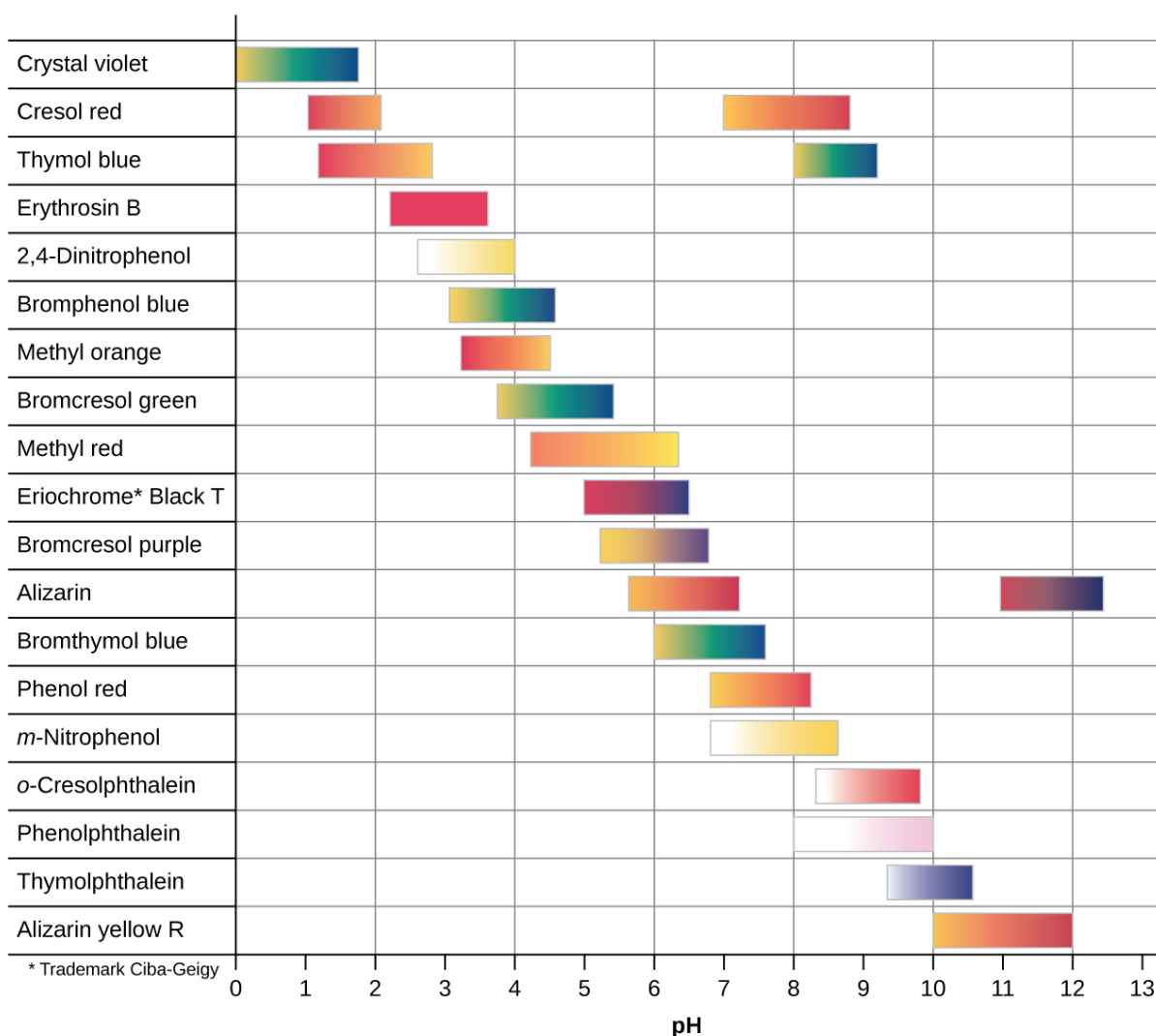
$$pH = pK_a + \log \left( \frac{[\text{In}^-]}{[\text{HIn}]} \right)$$

In solutions where  $pH > pK_a$ , the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When  $pH < pK_a$ , the log term must be

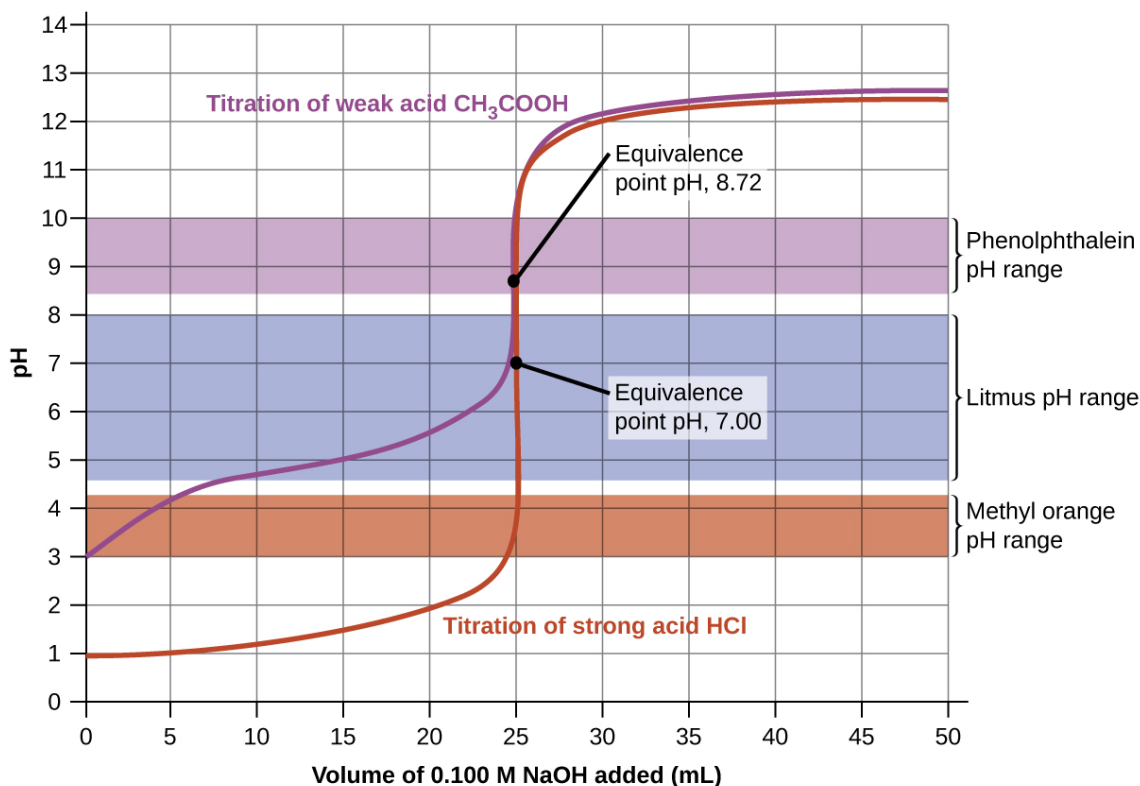


negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pK<sub>a</sub>, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The **color change interval** (or *pH interval*) for an acid-base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately pK<sub>a</sub> ± 1.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. [\[link\]](#) presents several indicators, their colors, and their color-change intervals.



This chart illustrates the color change intervals for several acid-base indicators.



Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The titration curves shown in [\[link\]](#) illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

The weak acid titration curve in [\[link\]](#) shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of

litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

## Key Concepts and Summary

The titration curve for an acid-base titration is typically a plot of pH versus volume of added titrant. These curves are useful in selecting appropriate acid-base indicators that will permit accurate determinations of titration end points.

### Exercise:

#### Problem:

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

---

#### Solution:

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

### Exercise:

#### Problem:

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

### Exercise:

#### Problem:

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ( $K_a = 9.8 \times 10^{-5}$ ) with 0.100 *M* KOH.

- (a) no KOH added
  - (b) 20 mL of KOH solution added
  - (c) 39 mL of KOH solution added
  - (d) 40 mL of KOH solution added
  - (e) 41 mL of KOH solution added
- 

#### Solution:

(a) pH = 2.50; (b) pH = 4.01; (c) pH = 5.60; (d) pH = 8.35; (e) pH = 11.08

**Exercise:****Problem:**

The indicator dinitrophenol is an acid with a  $K_a$  of  $1.1 \times 10^{-4}$ . In a  $1.0 \times 10^{-4}\text{-}M$  solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

**Glossary**

acid-base indicator

weak acid or base whose conjugate partner imparts a different solution color; used in visual assessments of solution pH

color-change interval

range in pH over which the color change of an indicator is observed

titration curve

plot of some sample property (such as pH) versus volume of added titrant

# The Periodic Table

Period	Group																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 <b>H</b> 1.008 hydrogen																	2 <b>He</b> 4.003 helium
2	3 <b>Li</b> 6.94 lithium	4 <b>Be</b> 9.012 beryllium											5 <b>B</b> 10.81 boron	6 <b>C</b> 12.01 carbon	7 <b>N</b> 14.01 nitrogen	8 <b>O</b> 16.00 oxygen	9 <b>F</b> 19.00 fluorine	10 <b>Ne</b> 20.18 neon
3	11 <b>Na</b> 22.99 sodium	12 <b>Mg</b> 24.31 magnesium											13 <b>Al</b> 26.98 aluminum	14 <b>Si</b> 28.09 silicon	15 <b>P</b> 30.97 phosphorus	16 <b>S</b> 32.06 sulfur	17 <b>Cl</b> 35.45 chlorine	18 <b>Ar</b> 39.95 argon
4	19 <b>K</b> 39.10 potassium	20 <b>Ca</b> 40.08 calcium	21 <b>Sc</b> 44.96 scandium	22 <b>Ti</b> 47.87 titanium	23 <b>V</b> 50.94 vanadium	24 <b>Cr</b> 52.00 chromium	25 <b>Mn</b> 54.94 manganese	26 <b>Fe</b> 55.85 iron	27 <b>Co</b> 58.93 cobalt	28 <b>Ni</b> 58.69 nickel	29 <b>Cu</b> 63.55 copper	30 <b>Zn</b> 65.38 zinc	31 <b>Ga</b> 69.72 gallium	32 <b>Ge</b> 72.63 germanium	33 <b>As</b> 74.92 arsenic	34 <b>Se</b> 78.97 selenium	35 <b>Br</b> 79.90 bromine	36 <b>Kr</b> 83.80 krypton
5	37 <b>Rb</b> 85.47 rubidium	38 <b>Sr</b> 87.62 strontium	39 <b>Y</b> 88.91 yttrium	40 <b>Zr</b> 91.22 zirconium	41 <b>Nb</b> 92.91 niobium	42 <b>Mo</b> 95.95 molybdenum	43 <b>Tc</b> [97] technetium	44 <b>Ru</b> 101.1 ruthenium	45 <b>Rh</b> 102.9 rhodium	46 <b>Pd</b> 106.4 palladium	47 <b>Ag</b> 107.9 silver	48 <b>Cd</b> 112.4 cadmium	49 <b>In</b> 114.8 indium	50 <b>Sn</b> 118.7 tin	51 <b>Sb</b> 121.8 antimony	52 <b>Te</b> 127.6 tellurium	53 <b>I</b> 126.9 iodine	54 <b>Xe</b> 131.3 xenon
6	55 <b>Cs</b> 132.9 cesium	56 <b>Ba</b> 137.3 barium	57-71 <b>La-Lu</b> *	72 <b>Hf</b> 178.5 hafnium	73 <b>Ta</b> 180.9 tantalum	74 <b>W</b> 183.8 tungsten	75 <b>Re</b> 186.2 rhenium	76 <b>Os</b> 190.2 osmium	77 <b>Ir</b> 192.2 iridium	78 <b>Pt</b> 195.1 platinum	79 <b>Au</b> 197.0 gold	80 <b>Hg</b> 200.6 mercury	81 <b>Tl</b> 204.4 thallium	82 <b>Pb</b> 207.2 lead	83 <b>Bi</b> 209.0 bismuth	84 <b>Po</b> [209] polonium	85 <b>At</b> [210] astatine	86 <b>Rn</b> [222] radon
7	87 <b>Fr</b> [223] francium	88 <b>Ra</b> [226] radium	89-103 <b>Ac-Lr</b> **	104 <b>Rf</b> [267] rutherfordium	105 <b>Db</b> [270] dubnium	106 <b>Sg</b> [271] seaborgium	107 <b>Bh</b> [270] bohrium	108 <b>Hs</b> [277] hassium	109 <b>Mt</b> [276] meitnerium	110 <b>Ds</b> [281] darmstadtium	111 <b>Rg</b> [282] roentgenium	112 <b>Cn</b> [285] copernicium	113 <b>Nh</b> [285] nihonium	114 <b>Fl</b> [289] flerovium	115 <b>Mc</b> [288] moscovium	116 <b>Lv</b> [293] livermorium	117 <b>Ts</b> [294] tennessine	118 <b>Og</b> [294] oganesson
				57 <b>La</b> 138.9 lanthanum	58 <b>Ce</b> 140.1 cerium	59 <b>Pr</b> 140.9 praseodymium	60 <b>Nd</b> 144.2 neodymium	61 <b>Pm</b> [145] promethium	62 <b>Sm</b> 150.4 samarium	63 <b>Eu</b> 152.0 europium	64 <b>Gd</b> 157.3 gadolinium	65 <b>Tb</b> 158.9 terbium	66 <b>Dy</b> 162.5 dysprosium	67 <b>Ho</b> 164.9 holmium	68 <b>Er</b> 167.3 erbium	69 <b>Tm</b> 168.9 thulium	70 <b>Yb</b> 173.1 ytterbium	71 <b>Lu</b> 175.0 lutetium
				89 <b>Ac</b> [227] actinium	90 <b>Th</b> 232.0 thorium	91 <b>Pa</b> 231.0 protactinium	92 <b>U</b> 238.0 uranium	93 <b>Np</b> [237] neptunium	94 <b>Pu</b> [244] plutonium	95 <b>Am</b> [243] americium	96 <b>Cm</b> [247] curium	97 <b>Bk</b> [247] berkelium	98 <b>Cf</b> [251] californium	99 <b>Es</b> [252] einsteinium	100 <b>Fm</b> [257] fermium	101 <b>Md</b> [258] mendelevium	102 <b>No</b> [259] nobelium	103 <b>Lr</b> [262] lawrencium

Atomic number → 1

Symbol → **H**

Atomic mass → 1.008

Name → hydrogen

Color Code			
<div></div>	Metal	<div></div>	Solid
<div></div>	Metalloid	<div></div>	Liquid
<div></div>	Nonmetal	<div></div>	Gas

## Essential Mathematics

### Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not equal to or greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

**Equation:**

$$\begin{aligned}1000 &= 1 \times 10^3 \\100 &= 1 \times 10^2 \\10 &= 1 \times 10^1 \\1 &= 1 \times 10^0 \\0.1 &= 1 \times 10^{-1} \\0.001 &= 1 \times 10^{-3} \\2386 &= 2.386 \times 1000 = 2.386 \times 10^3 \\0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1}\end{aligned}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example,  $1,230,000,000 = 1.23 \times 10^9$ , and  $0.00000000036 = 3.6 \times 10^{-10}$ .

### Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

**Example:**

**Adding Exponentials**

Add  $5.00 \times 10^{-5}$  and  $3.00 \times 10^{-3}$ .

**Solution**

**Equation:**

$$\begin{aligned} 3.00 \times 10^{-3} &= 300 \times 10^{-5} \\ (5.00 \times 10^{-5}) + (300 \times 10^{-5}) &= 305 \times 10^{-5} = 3.05 \times 10^{-3} \end{aligned}$$

**Subtraction of Exponentials**

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

**Example:**

**Subtracting Exponentials**

Subtract  $4.0 \times 10^{-7}$  from  $5.0 \times 10^{-6}$ .

**Solution**

**Equation:**

$$\begin{aligned} 4.0 \times 10^{-7} &= 0.40 \times 10^{-6} \\ (5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) &= 4.6 \times 10^{-6} \end{aligned}$$

**Multiplication of Exponentials**

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

**Example:**

**Multiplying Exponentials**

Multiply  $4.2 \times 10^{-8}$  by  $2.0 \times 10^3$ .

**Solution**

**Equation:**

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(3)} = 8.4 \times 10^{-5}$$

**Division of Exponentials**

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

**Example:**

**Dividing Exponentials**

Divide  $3.6 \times 10^5$  by  $6.0 \times 10^{-4}$ .

**Solution**

**Equation:**

$$\frac{3.6 \times 10^5}{6.0 \times 10^{-4}} = \left( \frac{3.6}{6.0} \right) \times 10^{(5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

**Squaring of Exponentials**

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

**Example:**

**Squaring Exponentials**

Square the number  $4.0 \times 10^{-6}$ .

**Solution**



**Equation:**

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

**Cubing of Exponentials**

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

**Example:****Cubing Exponentials**

Cube the number  $2 \times 10^4$ .

**Solution****Equation:**

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

**Taking Square Roots of Exponentials**

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

**Example:****Finding the Square Root of Exponentials**

Find the square root of  $1.6 \times 10^{-7}$ .

**Solution****Equation:**

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

## Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more reasonable if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no useful meaning in this situation. When reporting quantities, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

### Example:

#### Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

#### Solution

#### Equation:

$$\begin{array}{r} 4.\underline{383} \text{ g} \\ 0.\underline{0023} \text{ g} \\ \hline 4.\underline{385} \text{ g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

**Example:**

**Multiplication and Division with Significant Figures**

Multiply 0.6238 by 6.6.

**Solution**

**Equation:**

$$0.6238 \times 6.6 = 4.1$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

## The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm
1000	$10^3$	3
10	$10^1$	1
1	$10^0$	0
0.1	$10^{-1}$	-1
0.001	$10^{-3}$	-3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

**Equation:**

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is -1.4069, or

**Equation:**

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate  $10^x$  (where  $x$  is the logarithm of the number).

The natural logarithm of a number ( $\ln$ ) is the power to which  $e$  must be raised to equal the number;  $e$  is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

**Equation:**

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate  $e^x$  (where  $x$  is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.

**Equation:**

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

**Equation:**

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

**Equation:**

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

## The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

**Equation:**

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

**Equation:**

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

**Example:**

**Solving Quadratic Equations**

Solve the quadratic equation  $3x^2 + 13x - 10 = 0$ .

**Solution**

Substituting the values  $a = 3$ ,  $b = 13$ ,  $c = -10$  in the formula, we obtain

**Equation:**

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

**Equation:**

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

**Equation:**

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

# Two-Dimensional (x-y) Graphing

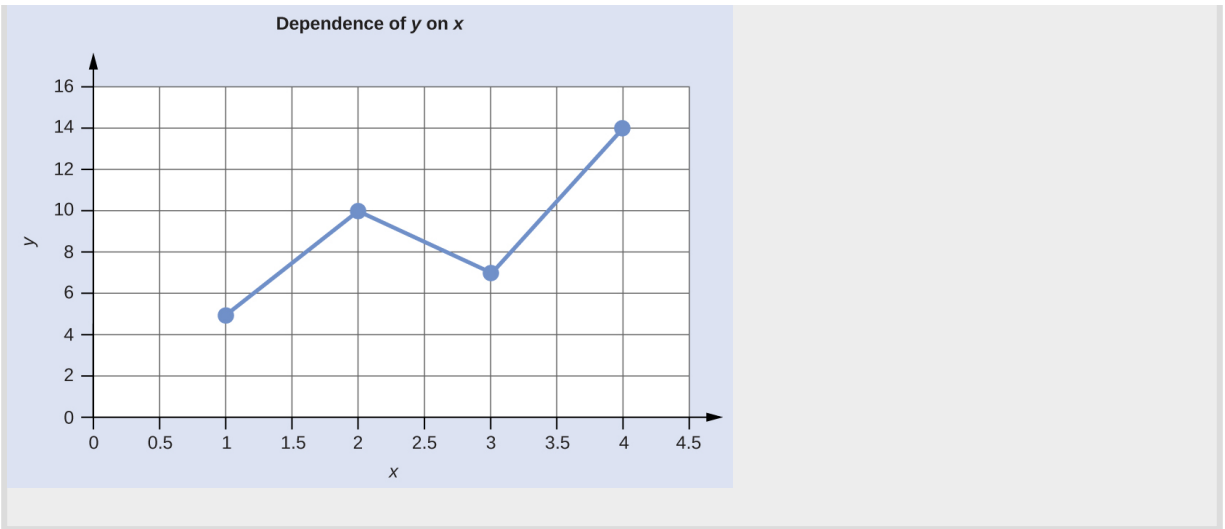
The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled ( $x$ ), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured ( $y$ ).

When the value of  $y$  is changing as a function of  $x$  (that is, different values of  $x$  correspond to different values of  $y$ ), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for ( $x,y$ ) data pairs.

**Example:**  
**Graphing the Dependence of  $y$  on  $x$**

$x$	$y$
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of  $y$  on  $x$ .



If the function that describes the dependence of  $y$  on  $x$  is known, it may be used to compute  $x, y$  data pairs that may subsequently be plotted.

**Example:**

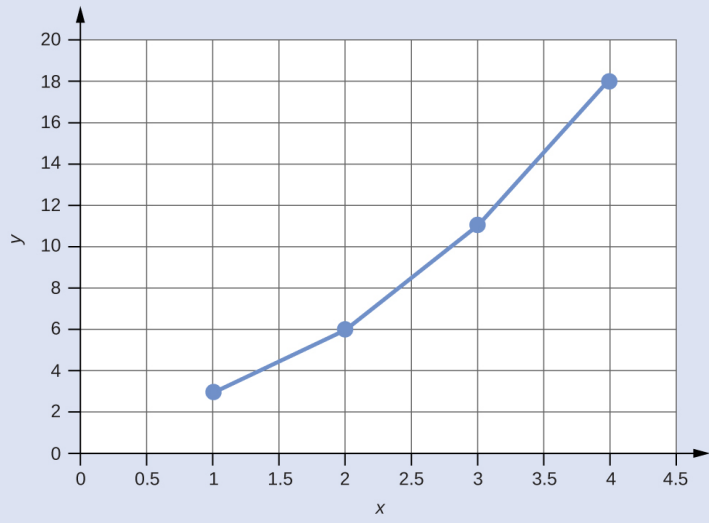
**Plotting Data Pairs**

If we know that  $y = x^2 + 2$ , we can produce a table of a few  $(x, y)$  values and then plot the line based on the data shown here.

$x$	$y = x^2 + 2$
1	3
2	6
3	11
4	18



$$y = x^2 + 2$$



## Units and Conversion Factors

Units of Length	
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)
centimeter (cm)	= 0.01 m (exact, definition)
millimeter (mm)	= 0.001 m (exact, definition)
kilometer (km)	= 1000 m (exact, definition)
angstrom (Å)	= $10^{-8}$ cm (exact, definition) = $10^{-10}$ m (exact, definition)
yard (yd)	= 0.9144 m
inch (in.)	= 2.54 cm (exact, definition)
mile (US)	= 1.60934 km

### Units of Volume

---

Units of Volume	
liter (L)	= 0.001 m <sup>3</sup> (exact, definition) = 1000 cm <sup>3</sup> (exact, definition) = 1.057 (US) quarts
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm <sup>3</sup> (exact, definition)
microliter μ	= 10 <sup>-6</sup> L (exact, definition) = 10 <sup>-3</sup> cm <sup>3</sup> (exact, definition)
liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
dry quart	= 1.1012 L
cubic foot (US)	= 28.316 L

Units of Mass	
gram (g)	= 0.001 kg (exact, definition)
milligram (mg)	= 0.001 g (exact, definition)
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb
ton (metric)	= 1000 kg (exact, definition) = 2204.62 lb

<b>Units of Mass</b>	
ounce (oz)	= 28.35 g
pound (lb)	= 0.4535924 kg
ton (short)	= 2000 lb (exact, definition) = 907.185 kg
ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

<b>Units of Energy</b>	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184 $10^7$ erg
erg	= $10^{-7}$ J (exact, definition)
electron-volt (eV)	= 1.60218 $10^{-19}$ J = 23.061 kcal mol <sup>-1</sup>
liter-atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J

Units of Energy	
British thermal unit (BTU)	<p>= 1054.804 J<sup>[<a href="#">footnote</a>]</sup></p> <p>BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.</p>

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	<p>= N m<sup>-2</sup> (exact, definition)</p> <p>= kg m<sup>-1</sup> s<sup>-2</sup> (exact, definition)</p>
atmosphere (atm)	<p>= 760 mm Hg (exact, definition)</p> <p>= 760 torr (exact, definition)</p> <p>= 101,325 N m<sup>-2</sup> (exact, definition)</p> <p>= 101,325 Pa (exact, definition)</p>
bar	<p>= 10<sup>5</sup> Pa (exact, definition)</p> <p>= 10<sup>5</sup> kg m<sup>-1</sup> s<sup>-2</sup> (exact, definition)</p>

## Fundamental Physical Constants

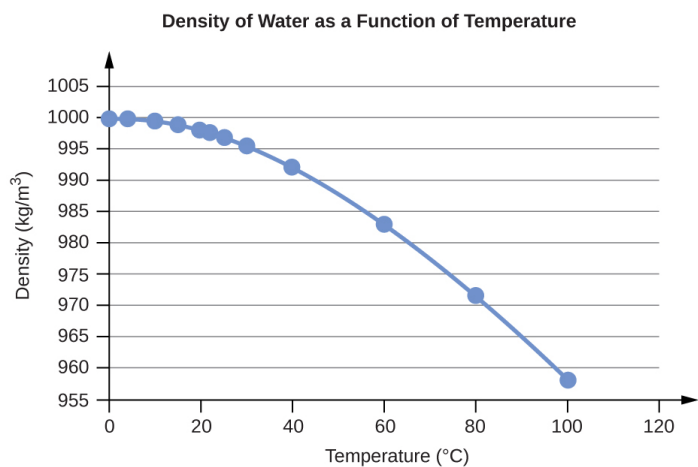
Fundamental Physical Constants	
Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27} \text{ kg}$
Avogadro's number	$6.02214076 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's constant ( $k$ )	$1.380649 \times 10^{-23} \text{ J K}^{-1}$
charge-to-mass ratio for electron ( $e/m_e$ )	$1.75881962 \times 10^{11} \text{ C kg}^{-1}$
fundamental unit of charge ( $e$ )	$1.602176634 \times 10^{-19} \text{ C}$
electron rest mass ( $m_e$ )	$9.1093897 \times 10^{-31} \text{ kg}$
Faraday's constant ( $F$ )	$9.6485309 \times 10^4 \text{ C mol}^{-1}$
gas constant ( $R$ )	$8.205784 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$
molar volume of an ideal gas, 1 atm, 0 °C	$22.41409 \text{ L mol}^{-1}$
molar volume of an ideal gas, 1 bar, 0 °C	$22.71108 \text{ L mol}^{-1}$
neutron rest mass ( $m_n$ )	$1.6749274 \times 10^{-27} \text{ kg}$

Fundamental Physical Constants	
Name and Symbol	Value
Planck's constant ( $h$ )	$6.62607015 \times 10^{-34} \text{ J s}$
proton rest mass ( $m_p$ )	$1.6726231 \times 10^{-27} \text{ kg}$
Rydberg constant (R)	$1.0973731534 \times 10^7 \text{ m}^{-1} =$ $2.1798736 \times 10^{-18} \text{ J}$
speed of light (in vacuum) ( $c$ )	$2.99792458 \times 10^8 \text{ m s}^{-1}$

Water Properties

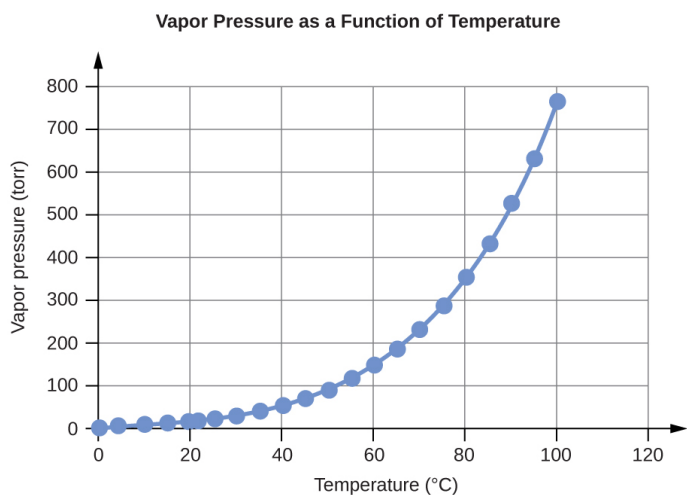
Water Density (g/mL) at Different Temperatures (°C)	
Temperature	Density (g/mL)
0	0.9998395
4	0.9999720 (density maximum)
10	0.9997026
15	0.9991026
20	0.9982071
22	0.9977735
25	0.9970479
30	0.9956502
40	0.9922
60	0.9832
80	0.9718
100	0.9584





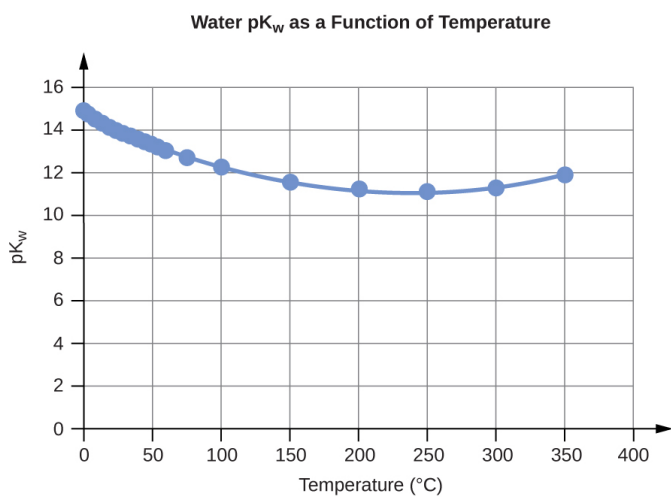
Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7



Water $K_w$ and $pK_w$ at Different Temperatures (°C)		
Temperature	$K_w \cdot 10^{-14}$	$pK_w$ <sup>[footnote]</sup> $pK_w = -\log_{10}(K_w)$
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84

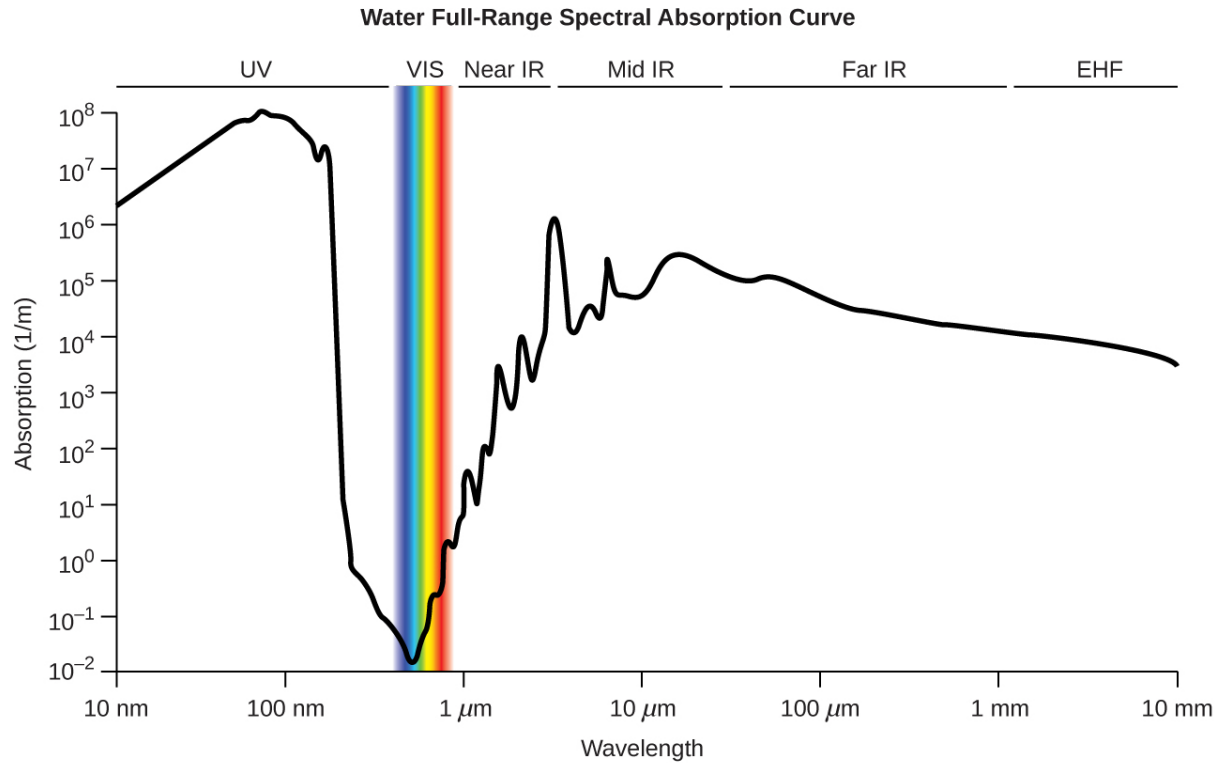
Water $K_w$ and $pK_w$ at Different Temperatures (°C)		
Temperature	$K_w \cdot 10^{-14}$	$pK_w$ <sup>[footnote]</sup> $pK_w = -\log_{10}(K_w)$
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25



Specific Heat Capacity for Water
$C^\circ(\text{H}_2\text{O}(l)) = 4.184 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$
$C^\circ(\text{H}_2\text{O}(s)) = 1.864 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$
$C^\circ(\text{H}_2\text{O}(g)) = 2.093 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	$\Delta H$ (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
$K_f = 1.86^\circ\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (cryoscopic constant)
$K_b = 0.51^\circ\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (ebullioscopic constant)



The plot shows the extent of light absorption versus wavelength for water. Absorption is reported in reciprocal meters and corresponds to the inverse of the distance light may travel through water before its intensity is diminished by  $1/e$  (~37%).

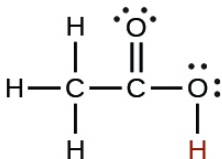
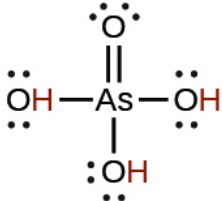
Composition of Commercial Acids and Bases

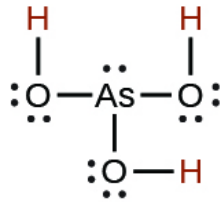
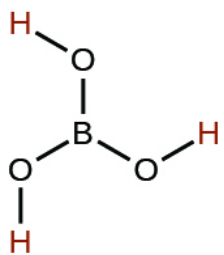
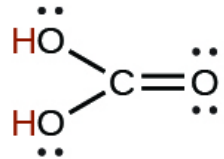
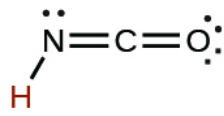
Composition of Commercial Acids and Bases			
Acid or Base <a href="#">[footnote]</a> Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.	Density (g/mL) <a href="#">[footnote]</a> This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4

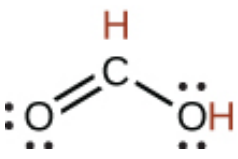

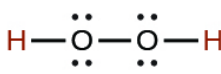
aqueous ammonia <a href="#">[footnote]</a> This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0



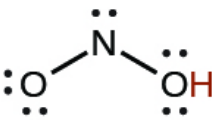
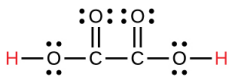
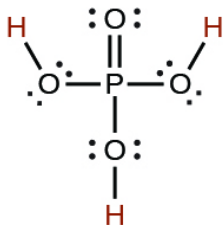
## Ionization Constants of Weak Acids

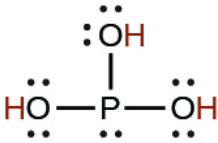
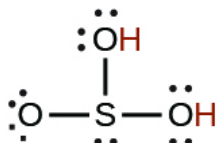
Ionization Constants of Weak Acids			
Acid	Formula	$K_a$ at 25 °C	Lewis Structure
acetic	$\text{CH}_3\text{CO}_2\text{H}$	$1.8 \times 10^{-5}$	
arsenic	$\text{H}_3\text{AsO}_4$	$5.5 \times 10^{-3}$	
	$\text{H}_2\text{AsO}_4^-$	$1.7 \times 10^{-7}$	
	$\text{HAsO}_4^{2-}$	$3.0 \times 10^{-12}$	

Ionization Constants of Weak Acids			
Acid	Formula	$K_a$ at 25 °C	Lewis Structure
arsenous	$\text{H}_3\text{AsO}_3$	$5.1 \times 10^{-10}$	
boric	$\text{H}_3\text{BO}_3$	$5.4 \times 10^{-10}$	
carbonic	$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	
	$\text{HCO}_3^-$	$4.7 \times 10^{-11}$	
cyanic	$\text{HCNO}$	$2 \times 10^{-4}$	

Ionization Constants of Weak Acids			
Acid	Formula	$K_a$ at 25 °C	Lewis Structure
formic	$\text{HCO}_2\text{H}$	$1.8 \times 10^{-4}$	
hydrazoic	$\text{HN}_3$	$2.5 \times 10^{-5}$	
hydrocyanic	$\text{HCN}$	$4.9 \times 10^{-10}$	
hydrofluoric	$\text{HF}$	$6.4 \times 10^{-4}$	
hydrogen peroxide	$\text{H}_2\text{O}_2$	$2.4 \times 10^{-12}$	
hydrogen selenide	$\text{H}_2\text{Se}$	$1.29 \times 10^{-4}$	
	$\text{HSe}^-$	$1 \times 10^{-12}$	

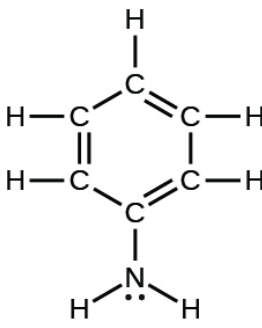
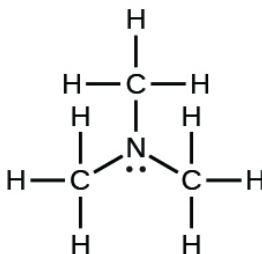
Ionization Constants of Weak Acids			
Acid	Formula	$K_a$ at 25 °C	Lewis Structure
hydrogen sulfate ion	$\text{HSO}_4^-$	$1.2 \times 10^{-2}$	
hydrogen sulfide	$\text{H}_2\text{S}$	$8.9 \times 10^{-8}$	
	$\text{HS}^-$	$1.0 \times 10^{-19}$	
hydrogen telluride	$\text{H}_2\text{Te}$	$2.3 \times 10^{-3}$	
	$\text{HTe}^-$	$1.6 \times 10^{-11}$	
hypobromous	$\text{HBrO}$	$2.8 \times 10^{-9}$	
hypochlorous	$\text{HClO}$	$2.9 \times 10^{-8}$	

Ionization Constants of Weak Acids			
Acid	Formula	$K_a$ at 25 °C	Lewis Structure
nitrous	$\text{HNO}_2$	$4.6 \times 10^{-4}$	
oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$6.0 \times 10^{-2}$	
	$\text{HC}_2\text{O}_4^-$	$6.1 \times 10^{-5}$	
phosphoric	$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$	
	$\text{H}_2\text{PO}_4^-$	$6.2 \times 10^{-8}$	
	$\text{HPO}_4^{2-}$	$4.2 \times 10^{-13}$	
phosphorous	$\text{H}_3\text{PO}_3$	$5 \times 10^{-2}$	

Ionization Constants of Weak Acids			
Acid	Formula	$K_a$ at 25 °C	Lewis Structure
	$\text{H}_2\text{PO}_3^-$	$2.0 \times 10^{-7}$	
sulfurous	$\text{H}_2\text{SO}_3$	$1.6 \times 10^{-2}$	
	$\text{HSO}_3^-$	$6.4 \times 10^{-8}$	

## Ionization Constants of Weak Bases

Ionization Constants of Weak Bases		
Base	Lewis Structure	$K_b$ at 25 °C
ammonia	$\begin{array}{c} \cdot\cdot \\ \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$	$1.8 \times 10^{-5}$
dimethylamine	$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ &   & &   & \\ \text{H} & -\text{C} & - & \text{N} & -\text{C}-\text{H} \\ &   & & \cdot\cdot &   \\ & \text{H} & & & \text{H} \end{array}$	$5.9 \times 10^{-4}$
methylamine	$\begin{array}{ccccc} & \text{H} & & & \\ &   & & \cdot\cdot & \\ \text{H} & -\text{C} & - & \text{N} & -\text{H} \\ &   & &   & \\ & \text{H} & & \text{H} & \end{array}$	$4.4 \times 10^{-4}$

Ionization Constants of Weak Bases		
Base	Lewis Structure	$K_b$ at 25 °C
phenylamine (aniline)		$4.3 \times 10^{-10}$
trimethylamine		$6.3 \times 10^{-5}$



## Half-Lives for Several Radioactive Isotopes

Half-Lives for Several Radioactive Isotopes					
Isotope	Half-Life <sup>[footnote]</sup> y = years, d = days, h = hours, m = minutes, s = seconds	Type of Emission <sup>[footnote]</sup> <i>E.C.</i> = electron capture, <i>S.F.</i> = Spontaneous fission	Isotope	Half-Life <sup>[footnote]</sup> y = years, d = days, h = hours, m = minutes, s = seconds	Type of Emission <sup>[footnote]</sup> <i>E.C.</i> = electron capture, <i>S.F.</i> = Spontaneous fission
$^{14}_6\text{C}$	5730 y	$(\beta^-)$	$^{210}_{83}\text{Bi}$	5.01 d	$(\beta^-)$
$^{13}_7\text{N}$	9.97 m	$(\beta^+)$	$^{212}_{83}\text{Bi}$	60.55 m	$(\alpha \text{ or } \beta^-)$
$^{15}_9\text{F}$	$4.1 \times 10^{-22}$ s	$(p)$	$^{210}_{84}\text{Po}$	138.4 d	$(\alpha)$
$^{24}_{11}\text{Na}$	15.00 h	$(\beta^-)$	$^{212}_{84}\text{Po}$	$3 \times 10^{-7}$ s	$(\alpha)$
$^{32}_{15}\text{P}$	14.29 d	$(\beta^-)$	$^{216}_{84}\text{Po}$	0.15 s	$(\alpha)$
$^{40}_{19}\text{K}$	$1.27 \times 10^9$ y	$(\beta \text{ or } E.C.)$	$^{218}_{84}\text{Po}$	3.05 m	$(\alpha)$
$^{49}_{26}\text{Fe}$	0.08 s	$(\beta^+)$	$^{215}_{85}\text{At}$	$1.0 \times 10^{-4}$ s	$(\alpha)$
$^{60}_{26}\text{Fe}$	$2.6 \times 10^6$ y	$(\beta^-)$	$^{218}_{85}\text{At}$	1.6 s	$(\alpha)$
$^{60}_{27}\text{Co}$	5.27 y	$(\beta^-)$	$^{220}_{86}\text{Rn}$	55.6 s	$(\alpha)$
$^{87}_{37}\text{Rb}$	$4.7 \times 10^{10}$ y	$(\beta^-)$	$^{222}_{86}\text{Rn}$	3.82 d	$(\alpha)$
$^{90}_{38}\text{Sr}$	29 y	$(\beta^-)$	$^{224}_{88}\text{Ra}$	3.66 d	$(\alpha)$
$^{115}_{49}\text{In}$	$5.1 \times 10^{15}$ y	$(\beta^-)$	$^{226}_{88}\text{Ra}$	1600 y	$(\alpha)$
$^{131}_{53}\text{I}$	8.040 d	$(\beta^-)$	$^{228}_{88}\text{Ra}$	5.75 y	$(\beta^-)$
$^{142}_{58}\text{Ce}$	$5 \times 10^{15}$ y	$(\alpha)$	$^{228}_{89}\text{Ac}$	6.13 h	$(\beta^-)$
$^{208}_{81}\text{Tl}$	3.07 m	$(\beta^-)$	$^{228}_{90}\text{Th}$	1.913 y	$(\alpha)$
$^{210}_{82}\text{Pb}$	22.3 y	$(\beta^-)$	$^{232}_{90}\text{Th}$	$1.4 \times 10^{10}$ y	$(\alpha)$
$^{212}_{82}\text{Pb}$	10.6 h	$(\beta^-)$	$^{233}_{90}\text{Th}$	22 m	$(\beta^-)$
$^{214}_{82}\text{Pb}$	26.8 m	$(\beta^-)$	$^{234}_{90}\text{Th}$	24.10 d	$(\beta^-)$

$^{206}_{83}\text{Bi}$	6.243 d	( <i>E. C.</i> )	$^{233}_{91}\text{Pa}$	27 d	( $\beta^-$ )
$^{233}_{92}\text{U}$	$1.59 \times 10^5$ y	( $\alpha$ )	$^{242}_{96}\text{Cm}$	162.8 d	( $\alpha$ )
$^{234}_{92}\text{U}$	$2.45 \times 10^5$ y	( $\alpha$ )	$^{243}_{97}\text{Bk}$	4.5 h	( $\alpha$ or <i>E. C.</i> )
$^{235}_{92}\text{U}$	$7.03 \times 10^8$ y	( $\alpha$ )	$^{253}_{99}\text{Es}$	20.47 d	( $\alpha$ )
$^{238}_{92}\text{U}$	$4.47 \times 10^9$ y	( $\alpha$ )	$^{254}_{100}\text{Fm}$	3.24 h	( $\alpha$ or <i>S. F.</i> )
$^{239}_{92}\text{U}$	23.54 m	( $\beta^-$ )	$^{255}_{100}\text{Fm}$	20.1 h	( $\alpha$ )
$^{239}_{93}\text{Np}$	2.3 d	( $\beta^-$ )	$^{256}_{101}\text{Md}$	76 m	( $\alpha$ or <i>E. C.</i> )
$^{239}_{94}\text{Pu}$	$2.407 \times 10^4$ y	( $\alpha$ )	$^{254}_{102}\text{No}$	55 s	( $\alpha$ )
$^{239}_{94}\text{Pu}$	$6.54 \times 10^3$ y	( $\alpha$ )	$^{257}_{103}\text{Lr}$	0.65 s	( $\alpha$ )
$^{241}_{94}\text{Pu}$	14.4 y	( $\alpha$ or $\beta^-$ )	$^{260}_{105}\text{Ha}$	1.5 s	( $\alpha$ or <i>S. F.</i> )
$^{241}_{95}\text{Am}$	432.2 y	( $\alpha$ )	$^{263}_{106}\text{Sg}$	0.8 s	( $\alpha$ or <i>S. F.</i> )